

A Characterization and Evaluation of Coal Liquefaction Process Streams

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Section 1

EXECUTIVE SUMMARY

HTI RUN CMSL-9

CONSOL completed analyses of 81 feed and process stream samples from HTI bench Run CMSL-9. HTI liquefaction bench unit Run CMSL-9 (227-87) was operated with all-dispersed catalyst and Black Thunder Mine (Wyodak and Anderson seam) coal, with and without mixed plastics or high density polyethylene (HDPE) as coprocessing feedstocks. The dispersed catalysts used were Molyvan A and HTI's iron catalyst, a sulfated iron hydroxide.

- Each SOH product oil analyzed was found to contain sediment, which appears to consist of oxygenated hydrocarbons. Sediments were found previously only in SOH oils from Run POC-2. Although the origin of the sediments is unknown, both runs in which it was found used Black Thunder Mine coal and in-line hydrotreating of the product oil.
- SOH product oils from periods 8, 17, and 29 appeared noticeably less hydrogenated than those from other periods. Although this would be expected for period 8, in which the in-line hydrotreater was by-passed, reasons for less hydrogenation during the other two periods are not clear.
- Interstage (K-2 slurry) samples and recycle VSOH or PFL oils from coal-only periods of all-dispersed catalyst operation were significantly more aromatic, less hydroaromatic, and less paraffinic than corresponding oils from comparison periods of Runs CC-1 and CC-15, in which one or both reactors contained supported catalyst. The corresponding SOH oils from all-dispersed catalyst operation were more aromatic and less hydroaromatic than their counterparts in Runs CC-1 and CC-15. These differences reflect a lower degree of hydrogenation during the all-dispersed catalyst operations; however, other processing conditions, such as higher reactor temperatures, and higher space velocity, also may have contributed to these differences.
- Changes in properties of oil samples from Condition 6 through Condition 9 included a decrease in aromaticity, increase in paraffinicity, and a decrease in donor solvent quality of the distillate from the CAS bottoms stream. These changes represent increasing displacement of coal-derived components by plastic-derived components.

- The HDPE content of CAS bottoms, PFC, and VSB streams was measured using a new extraction procedure. Only trace quantities of HDPE-like material were extracted from corresponding samples from operating periods in which coal alone was the feedstock.
- When pressure filtration was used for solids separation with coal and plastics feedstocks, the recycle PFL contained 20-25% incompletely converted HDPE, found as tetrahydrofuran-insoluble material. Concentrations of HDPE in the CAS bottoms resids, 10 wt % in period 34, and 30 to 35 wt % in periods 38 and 41, seem to reflect differences in solids separation mode (vacuum still vs. pressure filter) and type of recycle (ashy vs. ash-free). During pressure filtration periods, very little HDPE was rejected with the filter cake (PFC); nearly all of the HDPE was recycled in the PFL stream.
- The estimated overall conversion of HDPE ranged from 69% to 86% during the run, comparable to the HDPE conversion obtained previously for Conditions 2, 4, and 5 of Run CMSL-8. This was accomplished at a higher space velocity and without benefit of supported catalyst, but at higher liquefaction temperatures in Run CMSL-9.
- Higher conversion of HDPE in Condition 7, in which vacuum distillation and ashy recycle were used, relative to Conditions 8 and 9, in which pressure filtration and ash-free recycle were used, suggests that use of ashy recycle may result in increased HDPE conversion.
- Plastic (presumably HDPE) appears to be an important source of n-paraffins in the SOHs and CAS bottoms distillates from the coal/plastics operating periods. Relative amounts of n-paraffins in the SOHs and CAS bottoms 850 °F distillates increase in the GC-MS total ion chromatograms according to the following trend: Conditions 1 and 6 (coal) < Condition 7 (coal/mixed plastics) < Condition 8 (coal/HDPE) and Condition 9 (coal/mixed plastics).
- The polystyrene liquefaction products ethylbenzene and cumene comprised 9-15 wt % of the SOHs from the coal/mixed plastics periods of operation. These components in the product represent about 50 wt % of the PS fed in those periods.

RESID REACTIVITY

The University of Delaware continues to make progress in the resid conversion studies in the short time batch reactor. Development of the resid conversion mathematical kinetic model also is progressing.

TECHNOLOGY TRANSFER

- A paper was presented at the DOE-PETC/AIST-NEDO Joint Technical Meeting in Sendai, Japan on October 18, 1995. The paper "Characteristics of Process Oils From HTI Coal/Plastics Co-Liquefaction Runs" by G. A. Robbins, S. D. Brandes, R. A. Winschel, and F. P. Burke appears as Appendix 5.
- A presentation was made by R. A. Winschel at the technical review meeting for the DOE Refining and End-Use Project in San Antonio, TX on November 14, 1995. The hand-outs of presentation "Inspection of Net Products of HTI Runs POC-1 and POC-2" appear as Appendix 6.

Section 2

INTRODUCTION

CONTRACT ACTIVITIES THIS PERIOD

- CONSOL completed analyses of 81 feed and process stream samples from HTI bench Run CMSL-9. HTI liquefaction bench unit Run CMSL-9 (227-87) was operated with all-dispersed catalyst and Black Thunder Mine (Wyodak and Anderson seam) coal, with and without mixed plastics or high density polyethylene (HDPE) as coprocessing feedstocks. The dispersed catalysts used were Molyvan A and HTI's iron catalyst, a sulfated iron hydroxide.
- Several resid reactivity tests were made using 45 mL microautoclaves. These tests will be used to establish procedures for future work.
- A visit was made to the University of Delaware to discuss the status of the project and to plan future work; the meeting report for that visit is appended to this report (Appendix 4).
- The University of Delaware continues to make good progress on the resid reactivity task; the Delaware quarterly report is appended to this report (Appendix 3).
- A paper was presented at the DOE-PETC/AIST-NEDO Joint Technical Meeting in Sendai, Japan on October 18, 1995. The paper "Characteristics of Process Oils From HTI Coal/Plastics Co-Liquefaction Runs" by G. A. Robbins, S. D. Brandes, R. A. Winschel, and F. P. Burke appears as Appendix 5.
- A presentation was made by R. A. Winschel at the technical review meeting for the DOE Refining and End-Use Project in San Antonio, TX on November 14, 1995. The hand-outs of presentation "Inspection of Net Products of HTI Runs POC-1 and POC-2" appear as Appendix 6.

ACTIVITIES IN PROGRESS

- Received this quarter from HTI's liquefaction program were a set of 17 samples from Run CMSL-11 and a set of 43 samples from Run PB-01. Samples are on hand from HTI Runs POC-1 and CMSL-10 and the Exxon program. Samples were requested this quarter from HTI Run PB-02 (Appendix 2). Our characterization priorities next quarter will be samples from HTI Runs CMSL-11 and PB-01.

- One process oil from the University of North Dakota's direct liquefaction program is being characterized at DOE's request.
- A method was devised to selectively extract and recover unconverted high density polyethylene (HDPE) from coal/plastics co-liquefaction process oils. In the method, soluble coal products are extracted with room temperature tetrahydrofuran, unconverted HDPE is extracted with hot decalin, and insoluble coal products are left as a residue. The method was applied to samples from HTI Run CMSL-9 this quarter. The detailed method and other applications will be reported next quarter.
- The University of Delaware's work on Task 1.4: Structure and Reactivity is directed toward selecting a baseline catalyst system for the program and completing the characterization of the feed resids for the modeling effort.
- In-house experimental work on Task 1.4: Structure and Reactivity is in progress to supplement the resid reactivity data being generated by the University of Delaware. A number of runs will be made to test the effectiveness of two different catalysts, Shell 324 supported Ni/Mo on alumina and molybdenum naphthenate. The University of Delaware will do the work-ups on the products of these tests using their filtration and TGA methods.

Section 3

RESULTS AND DISCUSSION

HTI RUN CMSL-9

HTI RUN CMSL-9 BACKGROUND

A diagram of HTI's bench unit 227 as configured for Run CMSL-9 (also known as Run 227-87) is shown in Figure 1.^{1,3} CONSOL analyzed samples from sample points representing recycle and product streams; most of the feed samples had been previously analyzed.^{1,2,4} The operating conditions and process performance summary for the run are given in Table 1.^{1,3} The feed during Run CMSL-9 was 100 wt % coal, or coal with 33 wt % to 50 wt % plastic (mixed or high density polyethylene, HDPE). The subbituminous feed coal was from the Black Thunder Mine, Wyodak and Anderson seams. The feed plastics consisted of HDPE or a mixture of high density polyethylene/polypropylene/ polystyrene (HDPE/PP/PS) in the proportion 40/33/27. HTI's feed analyses are given in Table 2. The liquefaction system consisted of three reactors, all backmixed: one half-volume catalyst pretreater reactor (K-1) was followed by a series of two full-volume liquefaction reactors (K-2 and K-3). The liquefaction reactor temperature configuration was low/high (in K-2/K-3), and the pretreater was operated at lower temperature (ca. 130-140 °C). Supported catalyst was not present in the liquefaction reactors, but dispersed Mo or Mo and Fe catalyst precursors were fed with the feed slurry to the pretreater reactor. An in-line fixed-bed reactor was used to hydrotreat the light distillate product oil. The start-up solvent was the same Tank 4 L-814 oil (mostly petroleum-derived, a small amount is coal-derived) used during Run POC-2 operations;^{1,2,4} its analysis is shown in Table 3.

In Conditions 1 through 6, HTI tested several variables associated with dispersed catalyst, using coal as the feed. Variables tested included Mo catalyst concentration, catalyst recycle, and use of sulfated hematite catalyst. Condition 6 was a tie point to an earlier Exxon test, nominally at the same conditions, but HTI and Exxon used different Mo and Fe catalysts. In Conditions 7 and 9, coal and mixed plastics were the feedstocks (33% plastics in Condition 7, 50% plastics in Condition 9). In Condition 8, coal and 33% HDPE were the feedstocks. During Conditions 7 through 9, the sulfated hematite catalyst was added, and the reactor temperatures were higher, in order to promote cracking of HDPE.

Because of limited filterability of the heavy liquefaction product, there was difficulty operating the pressure filter early in the run. As a consequence, after period 8 (still during Condition 2), the switch was made to vacuum distillation. The unit was operated with vacuum distillation through period 34

(end of Condition 7), at which point it was returned to pressure filtration for the last two Conditions (8 and 9). Because of the changes from period 8 to period 9, HTI used period 8 data to work up results listed for material balance period 9.

For Condition 4, period 19, in which all of the Mo catalyst was recycled and no fresh catalyst was used, the ashy recycle source was toluene-washed PFC from earlier periods. During other ashy recycle periods, CAS bottoms was the ashy recycle source.

HTI obtained a number of interesting results from Run CMSL-9.¹ The plant could be operated at relatively high space velocity with all-dispersed catalyst to achieve high overall plant throughput. Recycled dispersed Mo catalyst was found to be less active than fresh dispersed catalyst. Addition of the iron catalyst slightly improved process performance when a combination of fresh and recycled dispersed Mo catalyst was in use, and seemed to allow the resumption of filtration in place of vacuum distillation. Using different catalysts, but at otherwise the same conditions, HTI achieved better performance than a comparative Exxon test using all-dispersed catalyst. HTI attributed the better performance to use of their more-active iron catalyst, FeOOH/SO_4 .¹ In Run CMSL-9, plastics of up to 50% concentration in the feed were processed with good results. Relative to liquefying coal alone, co-processing coal with mixed plastics results in improved overall process performance, with improved hydrogen utilization. HTI reported synergism of liquefying plastics with subbituminous coal in terms of C_4 -524 °C distillate product yield. The poor reactivity of HDPE found during Run CMSL-8 was confirmed in Run CMSL-9. HTI concluded, however, that the reactivity of HDPE was improved when it was processed with other polymers. In Run CMSL-9, the in-line hydrotreating was very effective for producing excellent-quality distillate with less than 50 ppm each of sulfur and nitrogen.

PRIOR RUN BACKGROUND AND CURRENT ANALYTICAL OBJECTIVES

CONSOL previously analyzed process stream samples from HTI Run CMSL-8, in which coal alone and coal/plastics were liquefied. Some results obtained from characterization of samples from Run CMSL-8 coal/plastics operation are:^{5,6} (1) Polystyrene (PS) products were identified and quantified in distillate product oil, and high-density polyethylene (HDPE) appeared to be an important source of n-paraffins in the product oil and heavy distillates from coal/plastics co-liquefaction. (2) Incompletely converted high-density polyethylene (HDPE) was found as tetrahydrofuran (THF)-insoluble material in the ash-free-resid recycle stream. Complex phase behavior seemed to be associated with HDPE-derived material in resid-containing streams. (3) An upper limit for HDPE conversion was estimated for each Condition of Run CMSL-8. Results indicated that HDPE was less reactive than coal or resid, but that conversion was responsive to process changes. (4) Several analytical issues were addressed: identification and quantification of HDPE, application of coal

liquefaction work-up procedures to coal/plastics liquefaction, and measurement of the extent of plastics liquefaction. (5) Along with separation by tetrahydrofuran (THF) insolubility and identification by Fourier-transform infrared (FTIR) spectroscopy, field-ionization mass spectrometry (FIMS) showed some promise for identification and quantification of incompletely converted HDPE.

Specific analytical objectives of this work are to determine:

- the conversion and fate of the plastics feedstocks, relative to coal-only operation
- interactions of feedstocks, and differences among feedstocks
- how the use of plastics feedstocks affects product quality
- to what degree oil property differences reflect feedstock differences vs. other (process) condition changes, such as unit operations, temperature, space velocity, and catalyst variables
- specifically, the amount of incompletely converted HDPE in various streams and use of this information to estimate HDPE reactivity

ANALYSIS STRATEGY

An overall analytical plan for samples from Run CMSL-9 was presented in a previous quarterly technical report.⁵ HTI switched from solids separation by filtration to vacuum distillation early in the run, and then returned to filtration late in the run. There are difficulties in directly comparing vacuum still overheads (VSOHs) with pressure-filter liquids (PFLs), or vacuum still bottoms (VSBs) with pressure-filter cakes (PFCs), especially from coal/plastics liquefaction. This is because the unconverted HDPE is expected to be found in the PFL, but not in the VSOH (it melts and dissolves or disperses in the filtrate, but is non-distillable). For this reason, much of the analytical effort was concentrated on the continuous atmospheric still (CAS) bottoms samples obtained throughout the run. The CAS bottoms is the feed stream to both filtration and vacuum distillation, and thus, is a good sample for comparison.

ANALYSES PERFORMED

CONSOL received and analyzed 81 process stream samples from Run CMSL-9. Samples received which were labelled as either period 5B, 5, or 6A samples were considered to represent material balance period 5. Samples labelled with no letter suffix, such as period 5 or 19, are believed to represent daily composites. Letter suffixes A, B, or C designate specific 8-hour periods or operating shifts within a given day. HTI did not provide LO- numbers with all of the samples. Most samples were received in 1-quart or 1-gallon cans; SOH and ASOH samples were received in 1-quart plastic bottles, and some of these were transferred after arrival to glass containers. Some SOH samples consisted of two phases. Each lower phase was found to be water and contained only minor

amounts of hydrocarbon. Therefore, it was omitted from the analytical data tables, and the results reported are only from the upper phase.

A brief description of the Run CMSL-9 samples and analyses conducted as CONSOL's baseline characterization and selected special analyses is provided in Table 4. In this report, the samples will be referred to by the abbreviations given in Table 4, e.g., SOH for the product oil, PFL or VSOH for the recycle liquid, and PFC or VSB for the bottoms stream. The baseline analytical methods can be applied to many different kinds of samples, can be performed quickly, and have proven to be suitable for liquefaction process stream characterization. In addition to the routine laboratory analyses, non-routine characterization (such as FTIR characterization of certain samples) was performed, based on experience with coal/plastics liquefaction samples from previous runs. Selected CAS bottoms 850 °F⁺ resids and corresponding PFC or VSB samples were subjected to a hot decalin extraction and filtration procedure to recover incompletely converted HDPE. Briefly, each sample was extracted with THF, the THF insoluble fraction was extracted with hot decalin to dissolve HDPE, the decalin/HDPE solution was cooled to precipitate HDPE, and the recovered HDPE was extracted with THF to remove decalin. The extraction method was recently developed and tested, and will be reported in detail at a later time.

The polypropylene feedstock was subjected to proximate and ultimate analyses (Table 5). Samples of the other feeds had been previously analyzed.⁴

Each whole SOH and ASOH oil sample was analyzed by ¹H-NMR (Table 8) for proton distribution. Proton distributions were obtained by ¹H-NMR for the pyridine-soluble portion of feed slurry, K-1 slurry, K-2 slurry, PFL, PFC, and CAS bottoms whole samples (Table 9). The PFL and CAS bottoms whole samples were distilled (Table 6) to 320 °C pot/270 °C column/5 torr (850 °F/atm). The pyridine-soluble portion of each 850 °F⁺ resid was analyzed by ¹H-NMR (Table 11). The 850 °F⁺ distillation bottoms samples were extracted with tetrahydrofuran (Table 6). Selected THF-soluble extracts were analyzed by solubility fractionation (Table 7). From each THF-insoluble filter cake a sample was ashed, and the insoluble organic matter (IOM, also called unconverted coal, or UC) content was calculated by difference (Table 6). Each 850 °F⁻ distillate was analyzed by ¹H-NMR (Table 10).

Microautoclave tests were made at the modified equilibrium conditions (9 g solvent, 6 g standard coal, 750 °F, 30 min) with selected whole samples and their 850 °F⁻ distillates (Table 12). Microautoclave coal conversions were calculated with a correction for solids in the oils.

Whole PFC and VSB samples were extracted with tetrahydrofuran (THF) (Table 6). Each CAS bottoms resid THF-soluble extract was analyzed by solubility fractionation (Table 7). From each THF-insoluble filter cake a sample was ashed, and the insoluble organic matter content was calculated by difference. Selected THF insoluble filter cakes were inspected for HDPE using FTIR spectroscopy.

OVERVIEW OF RUN RESULTS

CONSOL analyses of feed samples are given in Table 5. These compare favorably with those reported by HTI (Table 2). Selected characteristics of major process streams are presented graphically in Figures 2 through 10, providing an overview of the run results that are detailed in Tables 6 through 13 and discussions to follow. Paraffinic proton distribution as measured by alkyl beta plus gamma proton content showed an inverse relationship with the aromaticity in the samples (compare Figures 2-3 with Figures 5-6). This type of relationship also was evident in most of the process stream data from Run CMSL-8.⁹

Conditions 1-6 (periods through period 29) primarily represent differences related to changing catalyst concentration and type during the coal-only portion of the run. However, during Condition 2, the vacuum still was substituted for pressure filtration. Associated with differences in the catalyst and solids separation conditions were also differences in the manner of the recycle (ashy or ash-free, and cake washed and recycled, or CAS bottoms recycled). In general, there was not much period-to-period difference between aromaticities of corresponding whole K-1 and K-2 slurries, CAS bottoms, and PFL or VSOH samples (Figure 3). This suggests that the effects of changing catalyst type or concentration within the ranges used were not large. However, the PFC/VSB aromaticities of whole samples from periods 5 and 19 were distinctly lower than those of the other coal-only periods. In these two periods, it appears that there was little difference in solids separation unit feed and product sample properties (as determined by proton distribution) through filtration in period 5 or vacuum distillation in period 19 (CAS bottoms was very similar to both PFL (or VSOH) and PFC (or VSB)). Note that whole samples analyzed by NMR are solids-free (dissolved in pyridine and filtered). HTI reported analytical differences between corresponding PFL and PFC samples, in contrast with these results. As noted below, the VSOH from period 19 is unusual, because it contains a significant amount of toluene. Perhaps other unidentified sampling problems resulted in the apparent similarity in proton distributions observed by CONSOL in the period 5 and period 19 solids separation feed and product stream samples.

Conditions 7, 8, and 9 (periods 30 through 41) comprised the coal/plastics portion of the run. Variables for this portion of the run were solids separation method, recycle method, and feedstocks

(type and concentration of plastics). Vacuum distillation was used in Condition 7 (periods 30 through 34), and pressure filtration was used in Conditions 8 and 9 (periods 35 through 41). Aromaticities of whole samples generally decreased as the run progressed from Condition 6 through Condition 9 (Figure 3). There were corresponding increases in paraffinic proton concentrations as this portion of the run progressed. Also, there was a decrease in asphaltene and preasphaltene concentrations in the CAS bottoms resid THF solubles, with an increase in the concentration of the oil fraction (Figure 7). It appears likely that these changes represent increasing displacement of coal-derived components with plastic-derived components, and appears to be consistent with improved hydrogen utilization in the coal/plastic periods. It is not clear to what extent system lag and possible buildup of relatively unreactive HDPE may contribute to the observed decline in aromaticity and increase in paraffinity. The microautoclave conversion of the distillate portion of the CAS bottoms samples from Conditions 6 through 9 decrease with run time (Figure 8), following the aromaticity trend. This is consistent with an increasingly paraffinic (non-donor) distillate. However, specific GC-MS results presented later on the concentration of n-paraffins in the CAS bottoms distillate do not exactly fit this trend. Paraffinity as measured by NMR is not strictly selective for n-paraffins.

There was a lot of period-to-period variation in the 850 °F distillate content of the whole K-2 slurry, CAS bottoms, and PFL or VSOH samples in Run CMSL-9 (Figure 2). Perhaps the very high distillate content of the PFL/VSOH from period 9 is related to operating difficulties and the transition from pressure filtration to vacuum distillation between periods 8 and 9. In general, reasons for the observed variation in distillate content of these samples are not readily apparent.

There is concern about the integrity of two of the CAS bottoms samples, since they were found to contain only traces of ash (Table 6, samples from periods 38 and 41).

DISPERSED CATALYST OPERATION

Results from coal-only dispersed catalyst operation in Run CMSL-9 were compared with data from other Black Thunder coal runs in which supported catalyst was used (Tables 13-14). Run CC-15 was operated in the thermal/catalytic configuration with Shell S-317 Ni/Mo supported extrudate catalyst in the second-stage reactor. The period of Run CC-15 used for this comparison (period 8, Condition 2) was made with a dispersed hydrous iron hydroxide catalyst precursor impregnated in the coal. Results also are compared with those of previous HRI CTSL bench unit Run CC-1, which was operated in the catalytic/catalytic configuration with Shell S-317 catalyst. Period 16 (Condition 4) of Run CC-1 was used for this comparison. The periods of Run CMSL-9 which were compared to periods of Run CC-1 and CC-15 were periods 5 and 29 (Conditions 1 and 6), in which

coal alone was the feedstock. Comparisons are made with the acknowledgment that differences in conditions, such as reactor temperatures, solids separation methods, space velocity, and recycle type would affect oil characteristics (Table 13). In particular, space velocity was approximately 50% higher in Run CMSL-9 than in Runs CC-1 and CC-15.³

Interstage and PFL or VSOH oils from all-dispersed catalyst operation in Run CMSL-9 were significantly more aromatic (25 to 31% vs. 15 to 20% aromatic protons), less hydroaromatic (12 to 13% vs 15 to 19% cyclic beta protons), and less paraffinic (29 to 36% vs. 39 to 49% alkyl beta plus gamma protons) than corresponding oils from comparison periods of Runs CC-15 and CC-1 (Table 14). Furthermore, the SOH oils from all-dispersed catalyst operation in Run CMSL-9 which were exposed to supported catalyst only in the in-line hydrotreater were more aromatic (9 to 16% vs ca. 6% aromatic protons), and less hydroaromatic (16 to 21% vs 22 to 24% cyclic beta protons) than corresponding oils from comparison periods of Runs CC-15 and CC-1 (Table 14). These differences reflect a lower degree of hydrogenation in the samples produced in the absence of supported catalyst in the liquefaction system. Factors other than dispersed catalyst use, such as higher reactor temperatures, and higher space velocities, may also have contributed to lower hydrogenation. Although these results indicate lower hydrogenation, HTI found SOHs from these periods of Runs CC-1 and CC-15 to be similar in H/C ratio and API gravity to the SOH from period 5 of Run CMSL-9.^{1,3}

Donor solvent quality (Table 14) was considerably lower in the whole recycle oil from period 5 of Run CMSL-9 (65%) than in the corresponding oils from Runs CC-1 and CC-15 (74 to 86%). Perhaps this reflects greater depletion of donors in the absence of supported catalyst, resulting from less regeneration of donor components of the solvent.

INTERSTAGE OIL PROPERTIES

By examining interstage oil properties in relation to those of other streams, it may be possible to learn about the progress of liquefaction through the reactor system. Generally the whole samples of K-1 slurry, K-2 slurry, CAS bottoms, and PFL or VSOH were very similar in aromaticity (Figure 3). Differences of ca. 8% aromatic protons were noted in some periods (19, 34, and 41), otherwise differences were ca. 3% aromatic protons. The similarity of these results through the system tends to suggest that the reactor system was equilibrated and well-mixed. One difference that is noted is that the CAS bottoms samples consistently contained more 850 °F⁻ distillate than did the corresponding K-2 slurry samples (Figure 2). Thus, distillate production took place in the second stage, even though we did not see a change in the apparent aromaticity as observed by ¹H-NMR. HTI found feed conversions to be 93-94%, based on the interstage samples, whereas the

conversions through the entire process were 95-97%. Our results seem to be consistent with high coal conversion in the K-2 slurry sample, as HTI results indicated.¹

TOLUENE FOUND IN PERIOD 19 VSOH

A high concentration of toluene in the period 19 VSOH sample from HTI Run CMSL-9 was found by proton NMR spectroscopy and gas chromatography-mass spectrometry (GC-MS).⁹ V. Pradhan of HTI was informed about the presence of toluene in this sample. He indicated that the origin may have been distillation of a toluene-washed filter cake. This seems to have resulted somehow from preparation and use of dry, toluene-washed pressure-filter cake (PFC) from earlier in the run as the source of recycled Mo catalyst during Condition 4 (periods 15-19).

CHARACTERISTICS OF SOHs AND CAS BOTTOMS DISTILLATES

Characterization of SOH Sediments from Run CMSL-9

Separator overhead oils (SOHs) from all of the coal-only and coal/plastic periods contained sediments; characterization of the sediments is reported here. FTIR spectroscopic characterization indicates that the sediment is primarily oxidized hydrocarbon species (hydroxyl, aromatic, aliphatic, and carbonyl features are noted). Sediment in the distillate product was previously observed in the coal/plastics period of Run POC-2; it was not found in SOHs from Run CMSL-8. Although the origin of the sediment is unknown, both runs in which it was found used Black Thunder Mine coal and in-line hydrotreating of the product oil.

Sediment samples were obtained from the ten SOH product oils produced during coal-only and coal/plastics operation of HTI Run CMSL-9. A sample of each sediment was obtained for characterization by filtration of the SOH through a silver membrane filter, followed by a hexane wash and vacuum drying overnight. The filter deposit was inspected visually under a microscopy and characterized in situ by diffuse reflectance FTIR.

Most of the FTIR spectra show features similar to the sediment found in Period 43 of Run POC-2. The FTIR spectra indicate oxidized hydrocarbon species (hydroxyl, aromatic, aliphatic, and carbonyl features). Because a large amount of sulfur was found previously in the Run POC-2 sediment, further work could include analysis by EDX methods to check the Run CMSL-9 samples for sulfur and other elements.

FTIR spectra, observations on spectral features, and observations from optical microscopic examination are given in Appendix 1.

SOH Product Characteristics and Effects of In-Line Hydrotreating

The separator overheads (SOHs) from most periods of Run CMSL-9 were consistently low in aromatic hydrogen and high in paraffinic hydrogen content (Figure 9). SOHs from periods 8, 17, and 29, however, exhibited higher concentrations of aromatic hydrogen and lower concentrations of paraffinic hydrogen than in the other periods. Period 8 was a period in which the in-line hydrotreater (HTU) was off-line. Reasons for the differences in the period 17 and 29 SOH samples are not clear. The color of the SOH sample from period 8 was much darker than in any other period, and the samples from periods 17 and 29 were darker than samples from many of the other periods. Paraffinic hydrogen concentration in the SOHs was higher during the periods of coal/plastics operation, Conditions 7, 8, and 9 (periods 34, 38, and 41). The paraffinic hydrogen concentration (Figure 10) was distinctly higher in ASOH samples from coal/plastics Conditions 7 and 8, periods 34 and 38 (no period 41 sample was available), relative to coal-only periods of the run. The ASOH stream is a feed stream to the in-line hydrotreater. The concentrations of aromatic and paraffinic hydrogen in ASOH samples were consistent in the coal-only periods (Figure 10).

Identification of PS and HDPE Products in SOHs and CAS Bottoms Distillates by GC-MS

SOHs and CONSOL 850 °F distillates from continuous atmospheric still bottoms (CAS bottoms) samples from two coal-only periods and the three coal/ plastics periods were characterized by gas chromatography-mass spectrometry (GC-MS, Figures 11 and 12). Relative amounts of n-paraffins in the oils appear to increase in the total ion chromatograms (Figures 11 and 12) according to the following trend: Conditions 1 and 6, periods 5 and 29 (coal) < Condition 7, period 34 (coal/mixed plastics) < Condition 8, period 38 (coal/HDPE) and Condition 9, period 41 (coal/mixed plastics). CAS bottoms 850 °F distillates from Conditions 8 and 9, (periods 38 and 41) contain such high concentrations of paraffins that other components appear as only minor peaks in the GC-MS chromatogram. Alkyl beta protons account for 41-47% of the hydrogen in the Condition 8 and 9 (period 38 and 41) SOHs and CAS bottoms distillates, as measured by ¹H-NMR (Tables 8 and 10). Thus, the GC-MS total ion chromatograms of SOH samples and CAS bottoms distillates show that replacing a portion of the coal with mixed plastics or HDPE dramatically increased the relative concentrations of n-paraffins in the samples. The n-paraffins in the SOH samples shown in Figure 11 appear to be consistent in molecular weight distribution, whereas in the CAS bottoms distillate samples (Figure 12), the distribution of n-paraffins produced during coal/plastics liquefaction periods (34, 38 and 41, Conditions 7-9) appears to be shifted to lower molecular weight (indicated by lower retention time) than of those produced with coal alone (Conditions 1 and 6, periods 5 and 29). Thus, plastic (presumably HDPE) appears to be an important source of the n-paraffins in the SOHs and CAS bottoms distillates from the coal/plastics operating periods.

Two peaks corresponding to ethylbenzene and cumene (isopropylbenzene) are marked in Figure 11 as "EB" and "C", respectively. These components are polystyrene (PS) liquefaction products. Cumene was not found in SOHs from the coal-only periods (Conditions 1 and 6, periods 5 and 29) or the coal/HDPE period (Condition 8, Period 38). Ethylbenzene was present in the SOH at less than 0.4% concentration in the coal-only periods (Conditions 1 and 6, periods 5 and 29) and the coal/HDPE period (Condition 8, period 38). In contrast with Run CMSL-8,^{5,6} in Run CMSL-9 there is no indication that PS products persisted in the SOH product from the coal/HDPE period.

The PS products were quantified by GC-MS and ¹H-NMR (Table 15). The area of the ethylbenzene and cumene peaks, as a percentage of the total ion chromatogram was used to estimate the concentration of these components in the SOHs. The alkylbenzene concentration of the SOHs was estimated (as ethylbenzene) by integration of the ¹H-NMR peak near 7.1 ppm. Based on these estimates, ethylbenzene and cumene constitute about 9-15 wt % of the coal/mixed plastic period SOHs (with the HTU in use), and ethylbenzene alone constitutes less than 0.4 wt % of the coal/HDPE or coal-only period SOHs. In Run CMSL-9, approximately 50% of the PS fed to the process can be accounted for as these alkylbenzene products. This is similar to the results obtained in Run CMSL-8,^{5,6} although the percentage PS accounted for in the product SOH is slightly higher in the Run CMSL-9 case.

CHARACTERISTICS OF CAS BOTTOMS AND PFLs

The period 38 CAS bottoms 850 °F⁺ distillation resid appeared to consist of two layers, but the layers were similar in appearance and not distinctly separable based on physical characteristics such as brittleness (i.e., they could not be easily separated by breaking). These materials are different from the distillation bottoms of PFLs from Run CMSL-8. In those samples, layers with distinctly different properties were observed to separate.⁵

The tetrahydrofuran (THF) insoluble portions of CAS bottoms 850 °F⁺ resid samples from periods 38 and 41 of the three Run CMSL-9 coal/plastics period samples were light in color and low in ash content. In contrast, the corresponding period 34 sample was mostly black in color, but was inhomogeneous in appearance, with tan-colored particles in addition to black ones. As described in the following section, an extraction procedure was used to measure the concentration of HDPE-like material in various Run CMSL-9 process stream samples from coal/plastics periods (Conditions 7, 8, and 9, periods 34, 38, and 41). Those results were consistent with these empirical observations: the CAS bottoms 850 °F⁺ resids were found to contain 10 wt % HDPE (Condition 7, period 34), and 30 to 35 wt % HDPE (Conditions 8 and 9, periods 38 and 41). On the basis of 850 °F⁺ resid THFI (THF insolubles), the period 34 sample contained 24 wt % HDPE, and the period

38 and 41 samples contained 91 to 97 wt % HDPE. These sample characteristics seem to reflect the solids separation and recycle techniques in use during the periods of the run in which the samples were produced. In Condition 7 (period 34), ashy solids, resid, distillate, and HDPE were recycled as CAS bottoms, but no HDPE was recycled in the VSOH stream. In Conditions 8 and 9 (periods 38 and 41), HDPE was selectively recycled in the PFL stream (discussed below), but no ash or other solids were recycled. Thus, the HDPE concentration was higher, and the color of the THF insolubles was lighter, in Conditions 8 and 9 (periods 38 and 41).

In general, the CAS bottoms samples from coal/plastics periods were lower in aromatic protons, lower in cyclic beta (hydroaromatic) protons, and higher in alkyl beta plus gamma protons (as a rough measure of paraffinic protons) than corresponding samples from coal-only periods. This is consistent with the paraffinic character of the CAS bottoms and with high hydrogen utilization when coal and plastics were fed.

The PFL samples from coal/mixed-plastics Conditions 8 and 9 (periods 38 and 41) of HTI Run CMSL-9 were found to contain about 20 to 25 wt % THF insolubles, presumed to be incompletely converted HDPE. The Condition 7 (period 34) VSOH sample was presumed to contain no HDPE. One to two weight percent of the PFCs (Conditions 8 and 9, periods 38 and 41), and 11 wt % in the VSB (Condition 7, period 34) were found to be HDPE by the method described below.

CHARACTERIZATION OF UNCONVERTED HDPE/CONVERSION OF HDPE

A hot filtration method was developed and tested for recovery of unconverted HDPE from coal/plastics liquefaction samples and was used to characterize selected samples from Run CMSL-9. Results are provided here; details of the method will be provided in a later report. The method is based on hot extraction and filtration of THF insolubles with decalin at 150 °C. HDPE is precipitated from the cooled decalin filtrate and then filtered and washed with THF. The product recovered by this method may consist of heavy waxes that are HDPE-like, and incompletely converted (but not necessarily unreacted) HDPE.

Results from HDPE extraction experiments performed with selected samples from coal-only and coal/plastics operating periods are given in Table 16. The low recovery of HDPE-like material from samples representing coal-only operation indicates that material of coal origin does not interfere to any significant degree with the determination of incompletely converted HDPE by this method in these samples. The analyses indicate that very little HDPE reported to the pressure filter cake (PFC, Conditions 8 and 9, periods 38 and 41), but is nearly all found in the recycle oil (PFL, same periods) stream. In Condition 7 (period 34), when vacuum distillation was used, the HDPE should all be

found in the vacuum still bottoms (VSB), since HDPE should be non-distillable (we did not examine the VSOH for HDPE). We obtained poor to excellent HDPE balances for Run CMSL-9 (Table 16) when we examined results obtained from the set of three CAS bottoms samples and three corresponding VSB or PFC samples from the coal/plastics periods of the run. CAS bottoms is the feed to vacuum distillation or pressure filtration. In Condition 7 (period 34), vacuum distillation was used; 101 wt % of the HDPE determined to be in the CAS bottoms sample was accounted for in the VSB. Results for Condition 7 (period 34) were poor until we applied an adjustment to HTI's material balance data (described below). In Conditions 8 and 9 (periods 38 and 41), pressure filtration was used. In these periods, less than 1 wt % of the HDPE in each of the CAS bottoms samples was found to be in the PFC, and the overall balance of HDPE was ca. 120 wt % (the remainder was found in the PFLs). Thus, the calculated HDPE balances for three sets of HTI Run CMSL-9 samples were 101% in Condition 7 (period 34) and ca. 120% in Conditions 8 and 9 (periods 38 and 41). Poor HDPE balances around the solids separation unit based on CONSOL hot decalin filtration data and HTI material balance data from Run CMSL-9 may reflect broader sampling problems, since the corresponding balances of tetrahydrofuran solubles, IOM, and ash also were poor (Table 17). Some of the solids separation feed (CAS bottoms) samples, in particular, seem to be non-representative of the actual plant streams (ash content appears to be too low for those from periods 38 and 41, Tables 3 and 17), making their integrity suspect. We have applied the HDPE extraction method to samples from HTI Run CMSL-8, with good overall results (to be reported later). Therefore, we do not believe that there is a problem with the HDPE extraction results, per se.

We calculated overall and single-pass HDPE conversions for Run CMSL-9, as was previously reported for Run CMSL-8,^{5,6} except that HDPE in PFC and CAS bottoms samples can now be included in the conversion calculations, as required. Previously, it was assumed that there was no HDPE in the PFC samples, because no method was available to measure the concentration of unconverted HDPE in those samples. As before, THF insolubles in the whole PFL were taken as a measure of HDPE in those samples.

CONVERSION OF HDPE DURING RUN CMSL-9

Introduction

CONSOL and others have found that high-density polyethylene (HDPE) is less reactive than coal and other plastics feedstocks toward liquefaction at conventional liquefaction conditions.^{1,5,6} Completely converted HDPE has been found as tetrahydrofuran- (THF-) insoluble material in recycle liquid streams in Runs POC-2, CMSL-8, and CMSL-9. Other resid-containing and solids-containing streams have exhibited unusual solubility and phase behavior in samples from Runs POC-2, CMSL-8, and CMSL-9. Conversions of HDPE were estimated for Run CMSL-8^{5,6} and found to be lower

than are typically observed for coal or resid conversions in direct liquefaction. The reactivity and fate of HDPE, and its possible conversion synergism with other polymers or with coal remain important technical issues for continued development of this technology. For these reasons, conversion of HDPE in Run CMSL-9 was addressed as a continuation of the work begun in estimating conversions in Run CMSL-8. A method is now available to determine the concentration of HDPE (or HDPE-like material) in ashy, solids-containing samples.

Both single-pass and overall conversions of HDPE during Run CMSL-9 were determined. As before, it was assumed that the HTI unit was operating at steady-state, that the amount of unconverted HDPE in the pressure-filter liquids (PFLs) was measurable as the amount of tetrahydrofuran- (THF-) insoluble material in the PFLs (i.e., that the PFL THF-insolubles are unconverted HDPE). It was also assumed that the amount of unconverted HDPE in the CAS bottoms resids and PFC and VSB samples was measurable as the amount of THF-insoluble, hot decalin-soluble material extractable from those samples.

During Run CMSL-9, PFL or VSOH was both a recycle stream and a liquid product. During Condition 7 (period 34), CAS bottoms was a recycle stream, and VSB was a product stream. PFC was a product stream during Conditions 8 and 9 (periods 38 and 41). Overall conversion is defined as fresh HDPE fed which is not present as unconverted HDPE in the net products; in overall HDPE conversion, recycled HDPE is considered an internal stream and does not need to be explicitly accounted for. The single-pass conversion of HDPE is a measure of the disappearance of both the recycled and fresh HDPE fed (recycled HDPE is explicitly accounted for). The conversion calculations require material balance data for the run periods examined and a measure of the amount of HDPE in the feed, recycle, and product streams for those periods.

Results

The estimated overall conversion of HDPE (Table 18) ranged from 69% to 86% during the run, lower than the 90% to 95% coal conversion and 80% to 85% resid conversion typically observed for coal liquefaction. These HDPE conversions are comparable to those obtained previously for Conditions 2, 4, and 5 (periods 11, 20, and 23) of Run CMSL-8. This was accomplished in Run CMSL-9 at a higher space velocity and without benefit of supported catalyst, but at higher liquefaction temperatures than in Run CMSL-8.

Because we found apparent inconsistencies in HTI vacuum distillation material balance data for Condition 7, (period 34) of Run CMSL-9, we adjusted the material balance based on other periods in Conditions 6 and 7. We based our Condition 7 (period 34) single-pass conversion on adjusted

material balance values (Tables 16 and 17). This adjustment raised our calculated HDPE balance around the vacuum still from 74% (unadjusted) to 101%, and improved our calculated individual balances of THF solubles, THF insolubles, IOM, and ash for Condition 7 (period 34).

The overall conversions of HDPE calculated for the coal/plastics periods of Run CMSL-9 were 86% for Condition 7 (period 34), and 69% to 73% for Conditions 8 and 9 (periods 38 and 41). The single-pass conversions of HDPE calculated were 58% for Condition 7 (period 34), 36% for Condition 8 (period 38), and 28% for Condition 9 (period 41). Condition 7 (period 34) differed in run configuration from the other two periods in that vacuum distillation and ashy recycle were used instead of pressure filtration and ash-free recycle. Coal and mixed plastics were fed in Conditions 7 and 9 (periods 34 and 41); in Condition 8 (period 38), coal and HDPE were fed. Condition 7 (period 34) HDPE conversion results for Run CMSL-9 were distinctly better than those of the other two periods, or of those in Run CMSL-8, evidently as a result of using vacuum distillation and ashy recycle. Perhaps the recycled catalyst enhanced cracking in Condition 7 (period 34). The conversions of HDPE in Conditions 8 and 9 (periods 38 and 41) of Run CMSL-9 were similar to, and perhaps slightly better than those in Conditions 2, 4, and 5 (periods 11, 20, and 23) of Run CMSL-8. HTI estimated overall conversions of HDPE to 524 °C material as 91%, 56%, and 66%, respectively, for Conditions 7, 8, and 9 (periods 34, 38, and 41) of Run CMSL-9.^{1,2} Our results were slightly lower for Condition 7, period 34 (86% vs. 91%), but higher for Condition 8, period 38 (69% vs. 56%) and Condition 9, period 41 (73% vs. 66%). HTI's estimates are based on fixed assumed conversions of 88% for coal resid, and 100% for PS and PP plastics, and correlation with actual conversions of the combined feeds.

Section 4

EXPERIMENTAL

HTI RUN CMSL-9

All samples analyzed for proton distribution by NMR spectroscopy were dissolved in 99.96% deuterated pyridine (whole or resid samples) or in CDCl_3 (distillate samples) and integrated electronically. The solids-containing whole samples were sonicated with deuterated pyridine and filtered for analysis by ^1H -NMR.

Response factors used for flame ionization detection of solubility fractions from all periods were those previously used for samples produced from Black Thunder Mine coal.

GC-MS analyses were done with a DB-5 column, 30 m x 0.25 mm, 0.25 μm film thickness. The carrier gas was He at 20 psig. The injection port was held at 300 $^\circ\text{C}$ and injections were made in the splitless mode. The mass spectrometer was scanned from 33 to 300 amu. Peak identifications were based on searches of the Wiley/NBS mass spectral library and retention times. For SOH and ASOH samples, injected neat, the GC conditions were: 5 min at 10 $^\circ\text{C}$, 2 $^\circ\text{C}/\text{min}$ to 100 $^\circ\text{C}$, 4 $^\circ\text{C}/\text{min}$ to 320 $^\circ\text{C}$, up to 20 min at 320 $^\circ\text{C}$. For CAS bottoms distillate samples, injected as one-percent solutions in tetrahydrofuran, the GC conditions were: 5 min at 35 $^\circ\text{C}$; 35 $^\circ\text{C}/\text{min}$ to 100 $^\circ\text{C}$, 4 $^\circ\text{C}/\text{min}$ to 320 $^\circ\text{C}$, up to 20 min at 320 $^\circ\text{C}$.

Other details of the sample work-up and analytical procedures have been presented elsewhere.^{10,11}

Section 5

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TABLE 1

HTI RUN CMSL-9 (227-87) PROCESS PERFORMANCE SUMMARY

Condition	1	2	3	4	5	6(d)	7	8	9
Period Number (a)	1-5	6-9(c)	10-15	16-19	20-24	25-29	30-34	35-38	39-41
Hours of Run (End of Period)	120	216	360	456	576	696	816	912	984
Feeds, wt %									
Coal	100	100	100	100	100	100	67	67	50
HDPE	0	0	0	0	0	0	13	33	20
Polypropylene	0	0	0	0	0	0	11	0	16.5
Polystyrene	0	0	0	0	0	0	9	0	13.5
Dispersed Catalyst, ppm									
Fresh Mo as Molyvan A	300	200	150	0	150	100	300	300	300
Recycled Mo	0	0	150	300	150	100	300	0	0
Fresh Fe as FeOOH/SO ₄	0	0	0	0	0	10000	10000	10000	10000
Stage 1 Feed Space Velocity kg coal/hr/m ³ reactor vol	680	666	659	664	678	666	669	709	669
Temperatures, °C									
Preheater (K-1)	304	302	302	303	302	305	318	316	315
K-2	444	444	445	443	444	440	448	448	449
K-3	449	450	450	449	449	449	459	461	462
Solids Separation(b)	PF	PF/VS	VS	VS	VS	VS	VS	PF	PF
Total Material Recovery, % gross	98.7	102.7	98.5	99.6	100.9	103.8	99.2	99.1	102.1
Estimated Normalized Yields, wt % Dry Feed									
C ₁ -C ₃ in Gases	10.96	10.55	12.08	9.30	10.74	9.23	8.18	7.45	7.31
C ₄ -C ₇ in Gases	4.30	4.25	4.96	4.10	4.71	4.66	4.51	4.65	5.44
IBP-177 °C	17.24	13.45	14.26	13.10	14.44	7.37	21.43	8.52	23.64
177-260 °C	12.15	13.07	14.62	11.79	14.20	15.64	14.87	10.32	11.54
260-343 °C	17.19	14.05	15.71	14.41	15.75	14.92	16.31	12.18	13.88
343-454 °C	10.22	12.48	6.77	7.45	6.26	12.44	11.41	18.31	13.26
454-524 °C	1.69	2.37	2.26	5.66	3.46	4.01	3.92	4.6	4.31
524 °C ⁺	3.70	5.18	5.78	10.21	7.88	7.35	2.16	16.14	8.61
Unconverted Feed	3.93	3.93	4.55	4.44	4.77	4.34	5.41	4.31	2.92
Water	15.23	14.77	13.22	15.58	12.76	14.96	10.26	10.5	7.15
CO _x	3.78	5.37	5.59	3.10	4.81	4.38	1.67	2.82	2.07
NH ₃	1.02	0.97	0.97	0.88	0.88	0.86	0.56	0.51	0.38
H ₂ S	0.03	-0.03	0.16	0.08	-0.17	-0.15	-0.05	-0.1	-0.04
Hydrogen Consumption	7.20	6.17	6.69	5.87	6.26	5.75	4.56	4.14	3.43
Process Performance, wt % MAF Feed									
Feed Conversion	95.8	95.8	95.2	95.2	95.1	96.1	95.3	95.5	97.0
524 °C ⁺ Conversion	91.9	90.3	89.0	84.4	86.6	87.6	92.1	78.7	88.1
C ₄ -524 °C Distillates	66.6	63.3	62.2	60.0	62.4	62.6	75.4	61.0	74.3

Source: Reference 1

- (a) Last period given is the sample and material balance work-up period for this condition. Samples were the best available, taken at the end of material balance periods that were usually three or more days in duration.
- (b) Solids Separation Method: PF-Pressure Filter, VS-Vacuum Still (vacuum distillation began in period 9).
- (c) Data from period 8 was used to evaluate the work-up Period 9.
- (d) Tie-point condition for comparison with Exxon dispersed catalyst Run RCLU-1, Condition 4 (yield periods 422-424).

TABLE 2
HTI ANALYSES OF COAL AND PLASTIC (a) FEEDSTOCKS
FOR RUN CMSL-9

Material	Black Thunder Mine Coal	HDPE	Polystyrene	Polypropylene
Moisture Content	10.1			
<u>Elemental, wt % Dry</u>				
Carbon	70.12	85.71	92.31	85.71
Hydrogen	5.11	14.29	7.69	14.29
Sulfur	0.35	0	0	0
Nitrogen	0.99	0	0	0
Oxygen (by diff.)	17.24	0	0	0
Ash. % Dry	6.19	0	0	0
H/C Atomic Ratio	0.88	2	1	2

(a) All three plastics were initially completely insoluble in either quinoline or cyclohexane.

Source: Reference 1.

TABLE 3

HTI ANALYSIS OF START-UP/MAKE-UP OIL FOR CMSL-9

HTI No.	L-814
API Gravity	0.4
<u>Elemental Analysis</u>	<u>wt %</u>
Carbon	88.96
Hydrogen	8.25
Sulfur	2.22
Nitrogen	0.19
<u>ASTM D-1160 Distillation, vol % off</u>	<u>°C</u>
0	309 (IBP)
5	351
10	374
20	394
30	409
40	426
50	437
60	449
70	467
80	507
84	524
<u>Fraction</u>	<u>wt %</u>
IBP-343 °C	5.00
343-454 °C	53.99
454-524 °C	22.18
524 °C ⁺	18.36
Loss	0.47
Aromatic Carbon, % of carbon	80.03
Cyclic Hydrogen, % of hydrogen	44.36

Source: Reference 1.

TABLE 4
CONSOL ANALYSES OF SAMPLES
FROM HTI COAL/PLASTICS CO-LIQUEFACTION RUN CMSL-9

Sample Description; Name (Abbrev.)	Periods	Technique & Information Sought (Refer to Key)
Feed Slurry	5,9,15,19,24,29,34,38,41	A
Pretreater Sample; K-1 Slurry	5,9,15,19,24,29,34,38,41	A
Interstage Sample (IS); K-2 Slurry	5,9,15,19,24,29,34,38,41	A,E,F,G; THFS - B; THFI - D3; Dist. - A,B,E; Resid - G; Resid THFS - A,B,H; Resid THFI - D2
Atmospheric Overheads; CAS Overheads or Atmospheric Still Overheads (ASOH)	5,8,9,15,17,19,24,29,34,38	A,B;C(Selected Samples)
Product Distillate; Separator Overheads (SOH)	5,8,9,15,17,19,24,29,34,38,41	A,B;C(Selected Samples),D1
Filtration or Vacuum Still Feed; CAS Bottoms	5,9,15,19,24,29,34,38,41	A,F,G; THFS - B; Dist. - A,B,C,E; Resid - G; Resid THFS - A,B,H; Resid THFI - D2
Recycle Oil; Pressure Filter Liquid (PFL) or Vacuum Still Overheads (VSOH)	PFL:5,38,41 VSOH:9*,15,19,24,29,34	A,E,F,G; THFS - B; THFI - D3; Dist. - A,B,E; Resid - G; Resid THFS - A,B,H; Resid THFI - D2
Solid Residue; Pressure Filter Cake (PFC) or Vacuum Still Bottoms (VSB)	PFC:5,38,41 VSB:9*,15,19,24,29,34	G; THFS - A,B,H; THFI - D2

* Pressure filtration was used in periods 6-8 and vacuum distillation was used in period 9.

Note: THFS = THF Soluble Fraction; THFI = THF Insoluble Fraction

KEY TO TECHNIQUES AND INFORMATION SOUGHT:

- A = ¹H-NMR for hydrogen distribution (7 classes), aromaticity (degree of hydrogenation), paraffinicity, hydrogen donors
- B = FTIR in THF solution for phenolic -OH content (planned, but not conducted as of report issue date)
- C = GC-MS for composition, carbon numbers of paraffins
- D = special analyses, see below
- E = microautoclave test with standard coal for donor solvent quality
- F = 850°F distillation for distillate content
- G = THF extraction and ash for resid, ash and IOM content, for coal and resid conversion
- H = solvent fractionation (oils, asphaltenes, preasphaltenes) for resid composition.

Special Analyses:

- D1 = inspect for and characterize sediment
- D2 = extract HDPE (selected periods)
- D3 = inspect for HDPE (selected periods)

TABLE 5
ANALYSES OF FEED SAMPLES
HTI Run CMSL-9

Feed Sample	HDPE	PS	PP	Black Thunder Mine Coal
Reference	4	4	This Report	4
Sample No.	LO-6459 (From Run POC-2)	LO-6458 (From Run POC-2)		LO-6416 (From Run POC-2)
Moisture, wt % As-Determined	a	a	a	11.91
Basis for Ash and Ultimate Analyses	As-Determined			Dry
Ash, wt %	0.02*	<0.01*	<0.01*	6.27* 4.97**
Ultimate Analysis, wt %				
Carbon	85.73	91.91	86.12	69.96
Hydrogen	14.40	7.30	14.42	4.66
Nitrogen	0.07	0.13	<0.01	0.97
Sulfur	0.01	0.01	0.02	0.45
Oxygen (by diff.)	-0.23*	0.65*	-0.56*	17.69* 18.99**
H/C Ratio by Weight	0.168	0.079	0.167	0.066
H/C Atomic Ratio	2.00	0.94	2.00	0.79

Note: Analyses performed by CONSOL R&D.

(a) Plastic samples were assumed to be free of moisture.

* SO₃-containing ash basis

** SO₃-free ash basis

TABLE 6

**COMPONENT DISTRIBUTION OF WHOLE SAMPLES
HTI RUN 227-87 CMSL-9**

Sample Type	Period	Condition	CONSOL No. 1621-33-	HTI No.	Component Wt % of Sample				
					850 °F- Dist.	THF- Soluble Resid	IOM	Ash	Total
PFL	5	1	391	LO-6572	54.2	42.4	0.7	0.1	97.4
PFL-VSOH	9	2	392	LO-6573	79.1	17.8	<0.1	<0.1	96.9
VSOH	15B	3	393	LO-6574	-	-	-	-	-
VSOH*	19B	4	461	-	-	-	-	-	-
VSOH	24B	5	462	-	-	-	-	-	-
VSOH	29B	6	463	-	-	-	-	-	-
VSOH	34B	7	464	-	-	-	-	-	-
PFL	38A	8	465	-	42.1	29.3	26.6	<0.1	98.0
PFL	41B	9	466	-	46.1	23.7	27.5	0.1	97.4
K-2 SLURRY	6A	1	397	LO-6578	41.9	44.7	7.1	5.9	99.6
K-2 SLURRY	9	2	398	LO-6579	51.4	34.7	7.2	6.4	99.7
K-2 SLURRY	15B	3	399	LO-6580	44.4	34.7	9.4	11.2	99.7
K-2 SLURRY	19B	4	456	-	-	-	-	-	-
K-2 SLURRY	24B	5	457	-	38.2	36.6	9.6	12.0	96.4
K-2 SLURRY	29B	6	458	-	-	-	-	-	-
K-2 SLURRY	34B	7	459	-	27.9	31.5	20.1	17.9	97.4
K-2 SLURRY	38A	8	460	-	39.7	26.9	31.2	1.5	99.3
PFC	5B	1	394	LO-6575	-	53.6(a)	20.6	25.8	100.0
PFC-VSB	9	2	395	LO-6576	-	66.9(a)	15.4	17.7	100.0
VSB	15B	3	396	LO-6577	-	45.8(a)	23.3	30.9	100.0
VSB	19B	4	444	-	-	42.2(a)	21.5	36.3	100.0
VSB	24B	5	445	-	-	42.2(a)	21.5	36.3	100.0
VSB	29B	6	446	-	-	51.0(a)	17.2	31.8	100.0
VSB	34B	7	447	-	-	42.1(a)	33.2	24.7	100.0
PFC	38A	8	448	-	-	17.6(a)	40.6	41.8	100.0
PFC	41B	9	449	-	-	37.5(a)	18.7	43.8	100.0
CAS BTMS	5B	1	378	LO-6559	57.2	35.5	3.0	2.9	98.6
CAS BTMS	9	2	379	LO-6560	62.5	29.3	3.1	3.6	98.5
CAS BTMS	15B	3	380	LO-6561	69.5	20.4	3.3	5.4	98.6
CAS BTMS	19B	4	467	-	48.0	27.7	9.4	13.0	98.1
CAS BTMS	24B	5	468	-	44.9	33.4	7.9	11.9	98.1
CAS BTMS	29B	6	469	-	48.6	29.5	6.3	12.2	96.6
CAS BTMS	34B	7	470	-	53.2	22.0	11.4	9.3	95.9
CAS BTMS	38A	8	471	-	43.1	17.2	37.2	0.2	97.7
CAS BTMS	41B	9	472	-	47.9	19.4	29.7	0.2	97.2

*Contains toluene

(a) Calculated by difference; whole sample was extracted, no distillation was performed.

TABLE 7
SOLUBILITY FRACTIONATION OF SAMPLES
HTI RUN 227-87 CMSL-9

Sample	Period	Condition	CONSOL No. 1621-33-	HTI No. LO-	Wt % Resid THF Solubles		
					Oils	Asph.	Preasph.
CAS Btms	5	1	424	6559	69.8	20.2	10.0
CAS Btms	9	2	425	6560	68.4	19.8	11.8
CAS Btms	15	3	426	6561	74.3	16.8	9.0
CAS Btms	19	4	-	-	70.0	21.4	8.6
CAS Btms	24	5	-	-	70.7	22.0	7.3
CAS Btms	29	6	501	-	69.8	22.1	8.1
CAS Btms	34	7	496	-	70.2	21.4	8.3
CAS Btms	38	8	497	-	77.4	16.2	6.4
CAS Btms	41	9	498	-	80.1	14.5	5.4

Determined using Black Thunder coal response factors: O = 0.3717, A = 0.1635, P = 0.4648.

TABLE 8

**PROTON DISTRIBUTION OF WHOLE ASH-FREE SAMPLES
HTI RUN 227-87 CMSL-9**

Sample Type	Period	Condition	CONSOL No. 1621-33-	HTI No. LO-	Proton Distribution, % of Protons						
					Cond Arom	Uncond Arom	Cyclic Alpha	Alkyl Alpha	Cyclic Beta	Alkyl Beta	Gamma
M/U OIL (L-814)	19B	4	401	6582	15.3	5.1	15.3	12.3	13.4	24.7	13.9
M/U OIL	24B	5	436	-	14.8	5.9	13.6	12.5	12.7	25.4	15.1
M/U OIL	29B	6	437	-	14.1	6.5	13.4	13.3	12.5	24.9	15.2
M/U OIL	34B	7	438	-	16.9	6.4	13.6	14.1	11.4	23.8	13.8
M/U OIL	38A	8	439	-	15.0	5.7	14.7	12.1	13.1	25.1	14.3
M/U OIL	41B	9	440	-	14.5	5.9	14.2	12.1	12.8	25.0	15.6
SOH	5B	1	381	6562	6.3	2.7	4.1	4.5	21.3	35.1	26.1
SOH	8	2	382	6563	5.4	10.4	8.7	11.8	15.8	28.8	19.1
SOH	9	2	383	6564	0.8	3.7	5.0	5.7	23.5	34.6	26.7
SOH	15B	3	384	6565	1.5	4.7	6.0	5.8	20.8	35.3	26.0
SOH	17B	4	385	6566	6.1	11.6	9.9	12.0	15.7	27.2	17.5
SOH	19B	4	473	-	1.5	4.5	6.5	6.1	23.7	33.2	24.5
SOH	24B	5	474	-	1.3	5.1	7.2	6.0	22.3	34.2	23.8
SOH	29B	6	475	-	4.9	10.9	9.8	10.9	16.0	29.2	18.3
SOH	34B	7	476	-	1.8	6.2	5.4	5.1	15.7	36.9	28.8
SOH	38A	8	477	-	0.7	2.6	4.1	4.4	17.4	45.6	25.2
SOH	41B	9	478	-	3.2	4.7	3.8	3.2	13.5	42.2	29.3
ASOH	5	1	386	6567	12.8	8.6	13.4	11.7	13.4	25.8	14.2
ASOH	8	2	387	6568	14.1	10.1	13.1	12.2	13.0	24.3	13.1
ASOH	9	2	388	6569	11.7	10.9	13.9	13.0	13.5	24.2	12.8
ASOH	15B	3	389	6570	11.9	11.1	14.5	12.4	13.7	22.9	13.7
ASOH	17B	4	390	6571	11.5	11.0	14.2	12.7	14.2	23.5	13.0
ASOH	19B	4	479	-	11.5	11.7	14.4	12.9	13.8	23.6	12.1
ASOH	24B	5	480	-	11.1	11.9	13.4	13.0	13.6	24.2	12.8
ASOH	29B	6	481	-	11.1	11.8	14.3	12.5	14.2	24.4	11.8
ASOH	34B	7	482	-	9.7	10.3	10.9	10.3	11.4	31.6	15.8
ASOH	38A	8	483	-	8.0	11.4	9.8	11.2	12.8	29.6	17.2
PFL	5	1	391	6572	20.1	9.9	16.6	11.8	11.9	20.1	9.5
PFL-VSOH	9	2	392	6573	18.0	10.4	16.1	12.3	12.6	20.6	9.9
VSOH	15B	3	393	6574	16.5	10.4	17.6	11.9	13.4	21.2	9.0
VSOH(a)	19B	4	461	-	17.2	15.1	15.2	13.7	11.5	18.3	9.1
VSOH	24B	5	462	-	16.1	10.9	16.2	11.7	12.9	21.4	10.8
VSOH	29B	6	463	-	13.8	11.2	14.5	11.6	13.0	24.0	11.9
VSOH	34B	7	464	-	13.0	13.7	12.0	8.9	10.1	30.5	11.8
PFL	38A	8	465	-	13.6	5.7	12.2	8.1	9.6	37.2	13.6
PFL	41B	9	466	-	10.9	5.5	9.8	5.9	7.7	46.4	13.9

(a) Contains toluene.

TABLE 9
PROTON DISTRIBUTION OF WHOLE ASHY SAMPLES
HTI RUN 227-87 CMSL-9

Sample Type	Period	Condition	CONSOL No. 1621-33-	HTI No. LO-	Proton Distribution, % of Protons						
					Cond Arom	Uncond Arom	Cyclic Alpha	Alkyl Alpha	Cyclic Beta	Alkyl Beta	Gamma
K-1 SLURRY	19B	4	450	-	18.4	8.4	15.9	10.5	12.4	23.5	10.8
K-1 SLURRY	24B	5	451	-	18.4	8.1	16.8	11.0	13.1	23.0	9.7
K-1 SLURRY	29B	6	452	-	17.1	6.9	15.5	14.7	12.4	23.2	10.2
K-1 SLURRY	34B	7	453	-	17.0	8.8	14.5	8.6	11.8	28.4	10.8
K-1 SLURRY	38A	8	454	-	16.2	4.9	14.3	8.7	11.1	33.3	11.5
K-1 SLURRY	41B	9	455	-	13.9	9.1	11.3	7.5	11.2	35.3	11.7
K-2 SLURRY	6A	1	397	6578	19.9	11.3	15.0	12.9	11.7	18.6	10.6
K-2 SLURRY	9	2	398	6579	20.3	9.2	17.2	11.7	12.2	20.0	9.5
K-2 SLURRY	15B	3	399	6580	18.1	9.1	17.1	10.7	12.8	21.5	10.6
K-2 SLURRY	19B	4	456	-	20.9	12.1	18.7	12.7	13.9	10.8	10.9
K-2 SLURRY	24B	5	457	-	18.7	10.6	16.2	11.4	12.8	20.1	10.2
K-2 SLURRY	29B	6	458	-	15.9	10.1	15.7	11.4	12.8	22.4	11.8
K-2 SLURRY	34B	7	459	-	13.5	7.9	12.8	8.1	10.6	32.0	15.1
K-2 SLURRY	38A	8	460	-	13.5	6.3	12.2	8.5	9.4	38.0	12.1
FEED SLURRY	5B	1	375	6556	19.3	6.3	16.7	11.0	12.7	23.0	11.0
FEED SLURRY	9	2	376	6557	18.5	7.7	16.4	11.1	12.4	23.1	10.8
FEED SLURRY	15B	3	377	6558	18.7	8.0	18.0	10.9	13.2	21.7	9.6
FEED SLURRY	19B	4	435	-	18.1	9.4	17.0	10.9	12.6	21.0	11.0
FEED SLURRY	24B	5	430	-	18.5	8.5	17.6	10.7	13.3	21.5	10.0
FEED SLURRY	29B	6	431	-	17.1	8.9	17.0	10.4	13.8	21.8	11.0
FEED SLURRY	34B	7	432	-	15.8	9.5	13.0	7.9	11.3	31.2	11.3
FEED SLURRY	38A	8	433	-	15.2	5.3	12.3	8.1	9.6	37.6	11.9
FEED SLURRY	41B	9	434	-	13.7	7.6	11.1	6.6	9.5	39.4	12.0
PFC	5B	1	394	6575	25.7	6.0	16.7	11.6	11.6	18.0	10.4
PFC-VSB	9	2	395	6576	35.2	7.5	19.8	9.5	11.2	10.4	6.4
VSB	15B	3	396	6577	43.6	4.9	18.7	8.6	10.3	9.1	4.6
VSB	19B	4	444	-	22.1	8.6	16.0	11.3	12.6	18.8	10.6
VSB	24B	5	445	-	40.5	7.5	17.4	8.9	10.0	9.8	5.8
VSB	29B	6	446	-	36.2	6.9	19.0	9.5	11.1	11.4	6.0
VSB	34B	7	447	-	39.8	6.8	15.2	7.6	8.5	15.8	6.4
PFC	38A	8	448	-	29.8	7.8	17.4	10.4	9.7	17.5	7.5
PFC	41B	9	449	-	26.6	7.5	15.2	9.1	9.1	22.9	9.7
CAS BTMS	5B	1	378	6559	20.7	9.8	16.5	11.8	11.9	19.2	10.1
CAS BTMS	9	2	379	6560	19.0	10.7	16.8	12.2	12.0	19.3	10.0
CAS BTMS	15B	3	380	6561	18.3	10.5	17.5	11.5	12.8	20.4	9.0
CAS BTMS	19B	4	467	-	18.6	10.7	17.3	11.6	12.8	19.6	9.3
CAS BTMS	24B	5	468	-	16.5	13.1	14.8	11.7	12.7	19.8	11.4
CAS BTMS	29B	6	469	-	17.3	11.2	16.4	11.2	12.9	21.0	10.2
CAS BTMS	34B	7	470	-	15.7	9.2	13.1	8.7	10.0	30.9	12.3
CAS BTMS	38A	8	471	-	12.4	6.3	9.7	7.4	7.9	43.5	12.8
CAS BTMS	41B	9	472	-	11.0	4.9	9.8	6.1	7.3	46.9	14.0

TABLE 10
PROTON DISTRIBUTION OF SAMPLE DISTILLATES
HTI RUN 227-87 CMSL-9

Sample Type	Period	Condition	CONSOL No. 1621-33-	HTI No. LO-	Proton Distribution, % of Protons						
					Cond Arom	Uncond Arom	Cyclic Alpha	Alkyl Alpha	Cyclic Beta	Alkyl Beta	Gamma
PFL	5	1	538	-	16.9	7.7	15.0	11.4	13.3	23.9	11.8
PFL-VSOH	9	2	540	-	16.6	9.9	15.7	12.3	12.7	22.4	10.4
PFL	38	8	534	-	13.4	5.4	12.2	8.4	10.1	39.5	11.1
PFL	41	9	536	-	9.4	4.7	9.6	6.5	9.7	46.6	13.4
K-2 SLURRY	6A	1	418	6578	18.3	8.3	14.6	12.2	11.8	22.4	12.4
K-2 SLURRY	9	2	420	6579	16.8	10.5	13.4	12.8	11.7	22.8	12.1
K-2 SLURRY	15	3	422	6580	15.0	9.4	14.9	11.2	12.9	23.8	12.7
K-2 SLURRY	19	4	546	-	16.7	9.2	16.4	11.7	13.4	22.5	10.1
K-2 SLURRY	24	5	544	-	16.3	9.7	14.9	11.8	12.7	23.1	11.4
K-2 SLURRY	34	6	542	-	15.7	7.9	14.0	9.6	12.0	28.2	12.6
K-2 SLURRY	38	7	485	-	12.9	6.7	11.2	9.1	10.0	37.4	12.7
CAS BTMS	5B	1	407	6559	15.9	9.6	14.6	11.9	9.6	26.1	12.3
CAS BTMS	9	2	414	6560	16.6	10.2	15.5	12.0	12.7	21.9	11.0
CAS BTMS	15	3	416	6561	15.8	10.7	16.0	11.4	13.1	22.5	10.6
CAS BTMS	19	4	527	-	15.8	10.4	16.1	11.7	13.0	22.4	10.6
CAS BTMS	24	5	513	-	14.8	10.6	15.9	12.3	14.8	21.1	10.6
CAS BTMS	29	6	499	-	15.1	9.9	16.6	11.4	13.8	23.6	9.6
CAS BTMS	34B	7	490	-	14.3	8.2	13.1	9.4	11.0	31.5	12.4
CAS BTMS	38A	8	492	-	11.7	6.0	10.9	8.5	9.9	41.2	11.9
CAS BTMS	41B	9	494	-	9.2	5.0	8.6	5.9	7.7	47.1	16.5

TABLE 11
PROTON DISTRIBUTION OF SAMPLE RESIDS
HTI RUN 227-87 CMSL-9

Sample Type	Period	Condition	CONSOL No. 1621-33-	HTI No.	Proton Distribution, % of Protons						
					Cond Arom	Uncond Arom	Cyclic Alpha	Alkyl Alpha	Cyclic Beta	Alkyl Beta	Gamma
PFL	5	1	539	-	32.2	8.0	17.5	10.9	10.9	12.6	7.8
PFL-VSOH	9	2	541	-	26.1	8.9	16.7	11.0	11.8	15.2	10.3
PFL	38	8	535	-	30.0	2.9	19.2	9.3	11.9	20.0	6.6
PFL	41	9	537	-	25.3	2.5	16.6	7.5	11.3	27.6	9.1
K-2 SLURRY	6A	1	419	LO-6578	-	-	-	-	-	-	-
K-2 SLURRY	9	2	421	LO-6579	-	-	-	-	-	-	-
K-2 SLURRY	15	3	423	LO-6580	-	-	-	-	-	-	-
K-2 SLURRY	19	4	547	-	29.6	6.0	19.9	10.0	12.4	14.7	7.5
K-2 SLURRY	24	5	545	-	28.2	7.9	17.8	10.1	12.0	15.2	8.7
K-2 SLURRY	34	6	543	-	28.7	7.0	17.9	9.4	12.4	16.3	8.3
K-2 SLURRY	38	7	486	-	-	-	-	-	-	-	-
CAS BTMS	5B	1	408	LO-6559	33.8	7.5	19.0	10.6	10.5	11.9	6.7
CAS BTMS	9	2	415	LO-6560	31.1	7.4	19.3	10.6	11.4	12.7	7.4
CAS BTMS	15	3	417	LO-6561	33.0	7.8	18.7	9.5	12.2	11.4	7.4
CAS BTMS	19	4	528	-	34.0	4.1	21.6	9.2	12.5	12.9	5.7
CAS BTMS	24	5	514	-	31.6	6.1	20.4	9.8	12.1	12.9	7.1
CAS BTMS	29	6	500	-	29.7	6.7	20.5	9.5	12.4	13.8	7.4
CAS BTMS	34B	7	491	-	32.2	5.1	19.5	8.7	11.3	16.4	6.7
CAS BTMS	38A	8	493	-	26.2	4.6	16.9	9.0	11.1	23.4	8.8
CAS BTMS	41B	9	495	227-87	25.2	3.8	15.9	7.6	10.9	27.7	8.9

TABLE 12
MICROAUTOCLAVE CONVERSIONS
HTI RUN 227-87 CMSL-9

Sample Type	Period	Condition	CONSOL No. 1621-33-	HTI No. LO-	Conversion, %	
					Whole Sample	850 °F-Dist.
PFL	5	1	391	6572	65.3	83.3
PFL-VSOH	9	2	392	6573	87.9	86.8
VSOH	15B	3	393	6574	-	-
VSOH (a)	19B	4	461	-	-	-
VSOH	24B	5	462	-	-	-
VSOH	29B	6	463	-	-	-
VSOH	34B	7	464	-	-	-
PFL	38A	8	465	-	55.5	64.8
PFL	41B	9	466	-	56.7	50.1
K-2 SLURRY	6A	1	397	6578	65.0	84.1
K-2 SLURRY	9	2	398	6579	76.2	87.9
K-2 SLURRY	15B	3	399	6580	77.4	88.5
K-2 SLURRY	19B	4	456	-	-	87.2
K-2 SLURRY	24B	5	457	-	-	85.5
K-2 SLURRY	29B	6	458	-	-	-
K-2 SLURRY	34B	7	459	-	-	82.0
K-2 SLURRY	38A	8	460	-	-	69.5
CAS BTMS	5B	1	378	6559	-	74.4
CAS BTMS	9	2	379	6560	-	-
CAS BTMS	15B	3	380	6561	-	-
CAS BTMS	19B	4	467	-	77.3	88.5
CAS BTMS	24B	5	468	-	81.1	85.1
CAS BTMS	29B	6	469	-	80.6	86.3
CAS BTMS	34B	7	470	-	68.4	80.1
CAS BTMS	38A	8	471	-	89.7	65.4
CAS BTMS	41B	9	472	-	69.0	53.2

(a) Contains toluene.

TABLE 13

**CONDITIONS OF RUN PERIODS CHOSEN FOR COMPARISON
OF SAMPLES FROM RUNS CC-1, CC-15, AND CMSL-9**

Run	CC-1	CC-15	CMSL-9	CMSL-9
Reference	7	8	This Report	This Report
Condition No.	4	2	1	6
Period (Day)	16	8	5	29
Catalyst Age, lb coal/lb cat	384	228	-	-
First-Stage Catalyst	Shell S-317	Dispersed Fe	Dispersed Mo	Dispersed Fe/Mo
Second-Stage Catalyst	Shell S-317	Shell S-317	-	-
First-Stage Temperature, °F	817	801	830	830
Second-Stage Temperature, °F	767	774	840	840
Relative Space Velocity (Ref. 3)	1.00	0.91	1.5(a)	1.5(a)

(a) Estimated.

TABLE 14

**COMPARISON OF SAMPLE PROPERTIES
FROM HTI RUNS CC-1, CC-15, AND CMSL-9**

Run Condition No./Period No.	CC-1 4/16	CC-15 2/8	CMSL-9 1/5	CMSL-9 6/29
<u>Whole Recycle Oil</u>	PFL	PFL	PFL	VSOH
Aromaticity (a), % of Protons	16.2	14.8	30.0	25.0
Hydroaromaticity (b), % of Protons	18.6	17.2	11.9	13.0
Paraffinicity (c), % of Protons	42.1	48.5	29.6	35.9
Phenolic -OH Concentration, meq/g Sample (* = calc'd from components, ** = actual)	0.14*	0.21**	-	-
Concentration of 850°F ⁺ Resid THFS, wt %	28.2	28.4	42.4	N/A
Donor Solvent Quality, % MAF Coal	86.0	80.3	65.3	N/A
Conversion in Mod-EQ Test				
<u>Whole INT</u>				
Aromaticity (a), % of Protons	20.4	19.6	31.2	26.0
Hydroaromaticity (b), % of Protons	16.7	15.3	11.7	12.8
Paraffinicity (c), % of Protons	39.1	43.5	29.2	34.2
Phenolic -OH Concentration, meq/g Sample (* = calc'd from components, ** = actual)	0.28*	0.61**		
Concentration of 850°F ⁺ Resid THFS, wt %	38.9	36.8	44.7	N/A
Donor Solvent Quality, % MAF Coal	80.6	73.9	65.0	N/A
Conversion in Mod-EQ Test				
<u>SOH</u>				
Aromaticity (a), % of Protons	6.6	5.6	9.0	15.7
Hydroaromaticity (b), % of Protons	24.2	22.2	21.3	16.0
Paraffinicity (c), % of Protons	55.2	62.3	61.2	47.5
Phenolic -OH Concentration, meq/g Sample	0.05	0.13	-	-

- (a) Defined as % condensed + uncondensed aromatic protons.
 (b) Defined as % cyclic beta protons.
 (c) Defined as % alkyl beta + gamma protons.

TABLE 15
QUANTITATION OF POLYSTYRENE LIQUEFACTION PRODUCTS
IN SOH PRODUCT OILS FROM HTI RUN CMSL-9

	Analysis by GC-MS, Area % of SOH Total Ion Chromatogram			Analysis by ¹ H-NMR		wt % PS in Dry Feed	SOH Yield, wt % of Dry Feed	EB+IPB by GC-MS, as wt % of PS Fed	EB by ¹ H-NMR, as wt % of PS Fed
	Ethylbenzene, Ret. Time ca. 16.7 min.	Cumene (Isopropylbenzene), Ret. Time ca. 21.8 min.	Total, Area % (assumed to equal wt % of SOH)	As Ethylbenzene, wt % from Integration of Peak at 7.1 ppm (a)					
Period									
5 (Coal)	0.33	N.D.	0.33	-	0	50.12	(b)	-	-
29 (Coal)	0.35	N.D.	0.35	-	0	35.05	(c)	-	-
34 (Coal/Mixed Plastics)	7.09	1.98	9.07	10.4	9	51.12	51.5	59.1	59.1
38 (Coal/HDPE)	0.13	N.D.	0.13	-	0	29.34	(d)	-	-
41 (Coal/Mixed Plastics)	11.38	2.37	13.75	14.6	13.5	48.69	49.6	52.7	52.7
8 (Coal - HTU Off-line)	0.40	0.04	0.44	-	0	40.39	(e)	-	-

(a) Used wt % H in SOH, as reported by HTI.¹

(b) Represents 0.2 wt % of dry coal fed; equivalent to 1.8 wt % of PS fed in period 34.

(c) Represents 0.1 wt % of dry coal fed; equivalent to 1.4 wt % of PS fed in period 34.

(d) Represents 0.04 wt % of dry coal fed; equivalent to 0.4 wt % of PS fed in period 34.

(e) Represents 0.2 wt % of dry coal fed; equivalent to 2.0 wt % of PS fed in period 34.

TABLE 16

HDPE EXTRACTION RESULTS AND MATERIAL BALANCES FOR SELECTED SAMPLES FROM COAL/PLASTICS OPERATIONS

Balances from HDPE Extraction Experiments									
Sample	Sample Wt % of Whole CAS Btms		Analysis, Wt % of Sample			Wt % of Whole CAS Btms			Total
	THFS	THF/DI	HDPE	THFS	THF/DI	HDPE			
Condition 6, Period 29 (Coal)									
CASB Resid	48.00	65.71	33.97	0.32	83.54	16.31	0.15		100.00
VSOH (diff)	70.00	100.00			70.00	0.00	0.00		70.00
VSU	30.00	51.21	48.62	0.17	15.36	14.59	0.05		30.00
Sums					85.36	14.59	0.05		100.00
Balances					102.18	89.45	33.20		100.00
Condition 7, Period 34 (Coal/Mixed Plastics)									
CASB Resid	42.70	58.72	31.46	9.82	82.37	13.43	4.19		100.00
VSOH (diff)	61.60*	100.00			61.60	0.00	0.00		61.60
VSU	38.40*	50.58	38.42	11.00	19.42	14.75	4.22		38.40
Sums					81.02	14.75	4.22		100.00
Balances					98.36	109.83	100.74		100.00
Condition 8, Period 38 (Coal/HDPE)									
CASB Resid	54.60	62.12	3.46	34.42	79.32	1.89	18.79		100.00
PFL	89.50	74.84		25.16	66.98	0.00	22.52		89.50
PFC	5.94	22.10	75.50	2.40	1.31	4.48	0.14		5.94
Sums					68.29	4.48	22.66		95.44
Balances					86.10	237.39	120.58		95.44
Condition 9, Period 41 (Coal/Mixed Plastics)									
CASB Resid	49.30	68.90	0.93	30.17	84.67	0.46	14.87		100.00
PFL	91.44	80.11		19.89	73.25	0.00	18.19		91.44
PFC	5.77	28.12	70.95	0.93	1.62	4.09	0.05		5.77
Sums					74.88	4.09	18.24		97.21
Balances					88.43	892.89	122.64		97.21

*Assumed split ratio differs from HTI material balance.

TABLE 17

**CONVENTIONAL EXTRACTION RESULTS AND MATERIAL BALANCES FOR SELECTED SAMPLES
FROM COAL/PLASTICS OPERATIONS**

Balances of Normal Workup Components											
Sample	Sample Wt % of Whole CAS Btms	Analysis, Wt % of Sample			Wt % of Whole CAS Btms						
		850 °F ⁻ Dist.	850 °F ⁺ Resid	IOM	Ash	850 °F ⁻ Dist.	850 °F ⁺ Resid	THFS	IOM	Ash	Total
Condition 6, Period 29 (Coal)											
CASB Resid	48.00	48.60	29.50	6.30	12.20	48.60	29.50	78.10	6.30	12.20	96.60
VSOH (diff)	70.00	100.00	0.00	0.00	0.00	70.00	0.00	70.00	0.00	0.00	70.00
VSB	30.00	0.00	51.00	17.20	31.80	0.00	15.30	15.30	5.16	9.54	30.00
Sums						70.00	15.30	85.30	5.16	9.54	100.00
Balances						144.03	51.86	109.22	81.90	78.20	103.52
Condition 7, Period 34 (Coal/Mixed Plastics)											
CASB Resid	42.70	53.20	22.00	11.40	9.30	53.20	22.00	75.20	11.40	9.30	95.90
VSOH (diff)	61.60*	100.00	0.00	0.00	0.00	61.60	0.00	61.60	0.00	0.00	61.60
VSB	38.40*	0.00	42.10	33.20	24.70	0.00	16.17	16.17	12.75	9.48	38.40
Sums						61.60	16.17	77.77	12.75	9.48	100.00
Balances						115.79	73.48	103.41	111.83	101.99	104.28
Condition 8, Period 38 (Coal/HDPE)											
CASB Resid	54.60	43.10	17.20	37.20	0.20	43.10	17.20	60.30	37.20	0.20	97.70
PFL	89.50	74.84	0.00	25.16	0.00	66.98	0.00	66.98	22.52	0.00	89.50
PFC	5.94	0.00	17.60	40.60	41.80	0.00	1.05	1.05	2.41	2.48	5.94
Sums						66.98	1.05	68.03	24.93	2.48	95.44
Balances						155.41	6.08	112.81	67.02	1241.46	97.69
Condition 9, Period 41 (Coal/Mixed Plastics)											
CASB Resid	49.30	47.90	19.40	29.70	0.20	47.90	19.40	67.30	29.70	0.20	97.20
PFL	91.44	80.11	0.00	19.89	0.00	73.25	0.00	73.25	18.19	0.00	91.44
PFC	5.77	0.00	37.50	18.70	43.80	0.00	2.16	2.16	1.08	2.53	5.77
Sums						73.25	2.16	75.42	19.27	2.53	97.21
Balances						152.93	11.15	112.06	64.87	1263.63	100.01

*Assumed split ratio differs from HTI material balance.

TABLE 18

HDPE CONVERSION IN HTI RUN CMSL-9

Overall Conversion of HDPE									
Period	HDPE in, wt % Dry Feed	PFL Product, wt % Dry Feed	wt % HDPE in PFL	PFC Product, wt % Dry Feed	wt % HDPE in PFC	HDPE Product, wt % Dry Feed	Overall Conv., %		
34	13.0	26.48	0.0	16.13	11.00	1.8	86.4		
38	33.0	40.04	25.2	11.61	0.14	10.1	69.4		
41	20.0	27.56	19.9	11.68	0.05	5.5	72.6		
Single-Pass Conversion of HDPE									
Period	Fresh HDPE Feed, g/h	Based on PFC and PFL Only			wt % HDPE in CASB	Based on CASB, PFC and PFL			
		Recycle HDPE In, g/h	Total HDPE In, g/h	HDPE Out, g/h		1-Pass Conv., %	Recycle HDPE In, g/h, w/CASB	Total HDPE In, g/h, w/CASB	1-Pass Conv., %
34	173.9	69.8	243.7	102.3	58.0	4.19	69.2	243.1	57.9
38	468.7	514.1	982.8	632.4	35.6	18.79	514.1	982.8	35.6
41	268.0	435.0	702.9	503.0	28.4	14.87	435.0	702.9	28.4

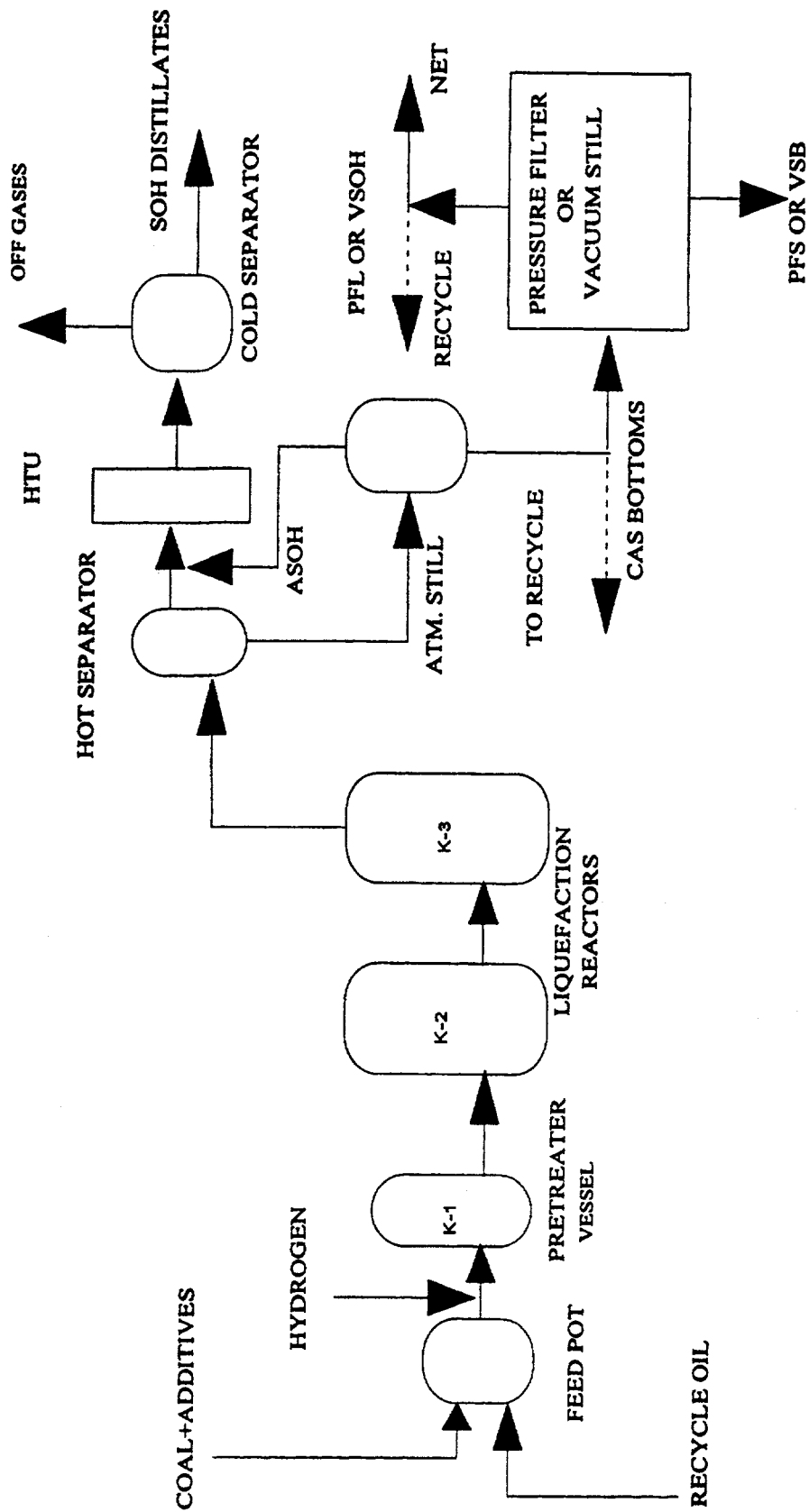


Figure 1. Simplified Schematic of Bench Unit Configuration - Run CMSL-9.

HTI RUN CMSL-9

DISTILLATE, WT. %

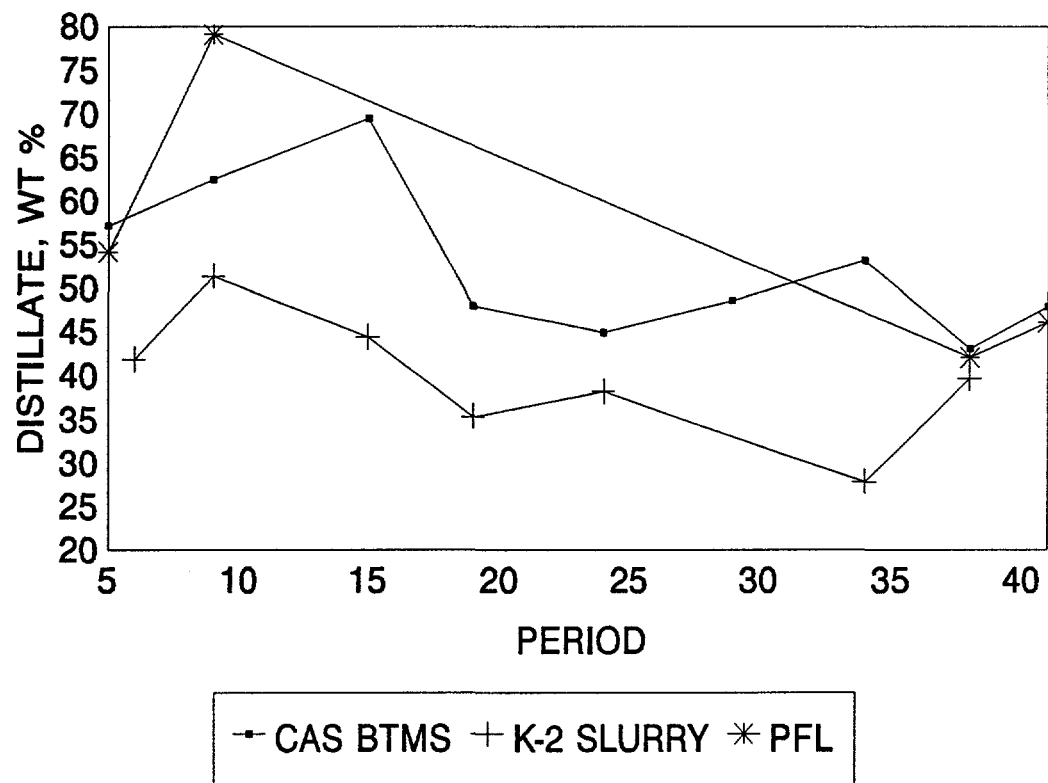


Figure 2. Distillate Content of Selected Process Streams During HTI Run CMSL-9.

HTI RUN CMSL-9

AROMATICS- WHOLE SAMPLES

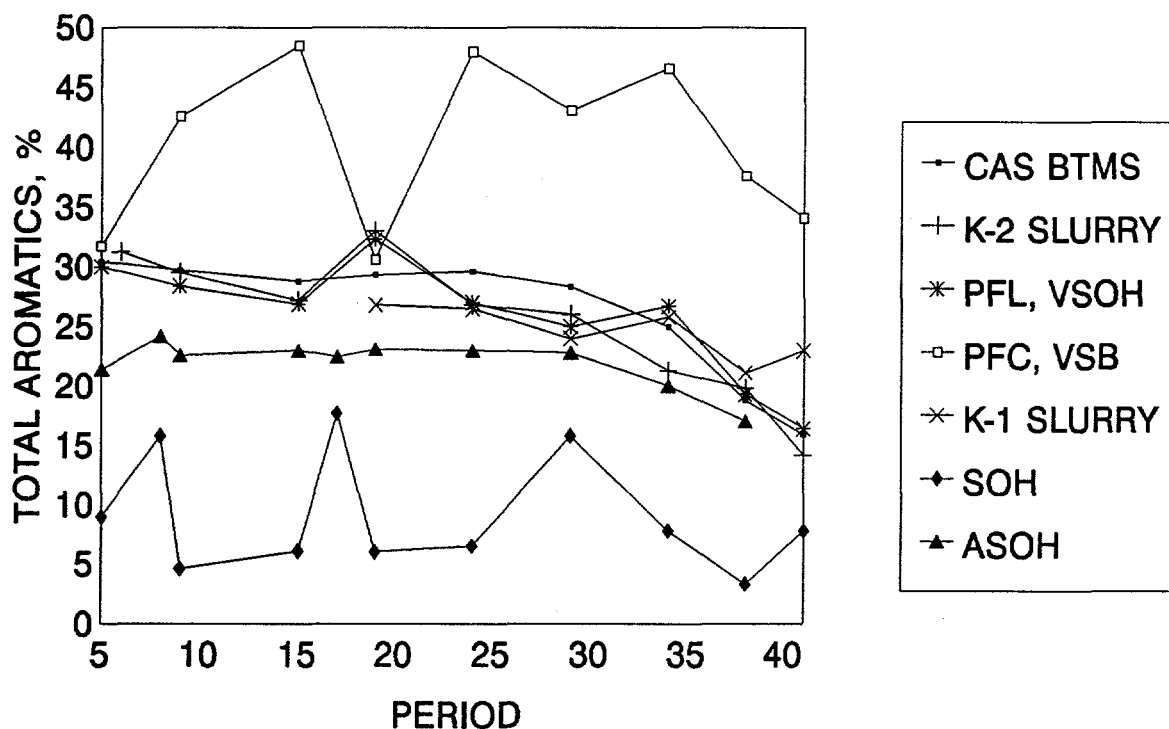


Figure 3. Proton Aromaticity of Whole Process Stream Samples During HTI Run CMSL-9.

HTI RUN CMSL-9

CAS BOTTOMS AROMATICS-WHOLE SAMPLES

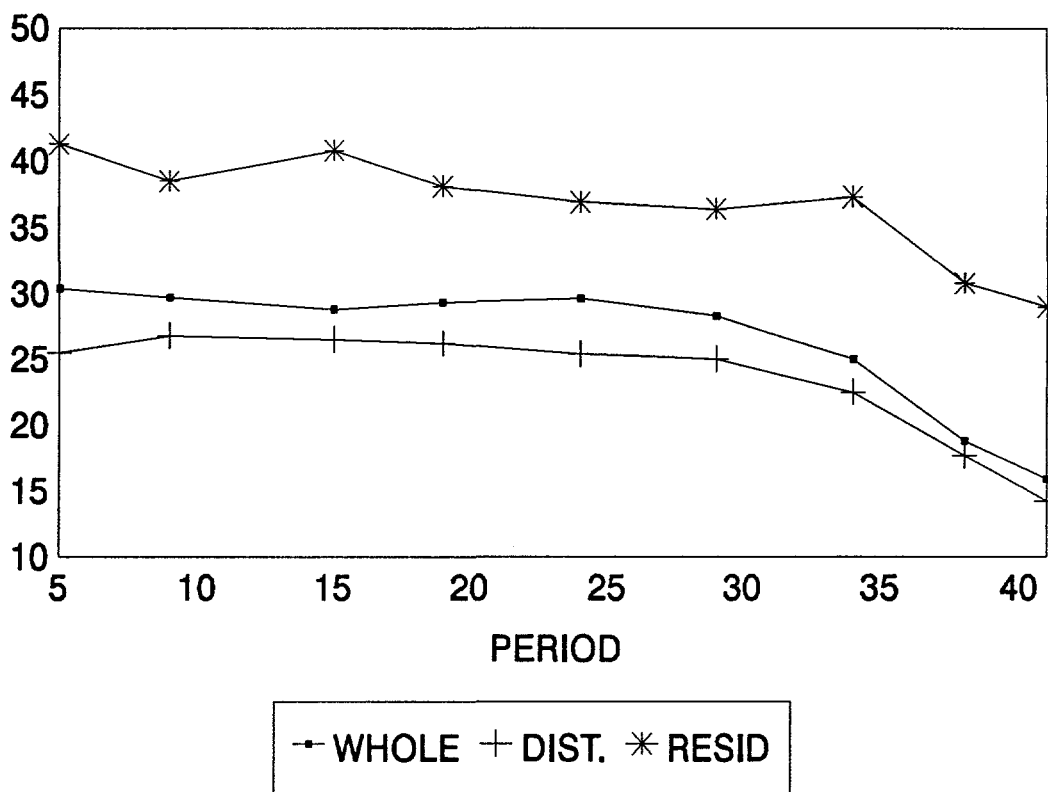


Figure 4. Proton Aromaticity of Whole CAS Bottoms, CAS Bottoms Distillate, and CAS Bottoms Resid Samples During HTI Run CMSL-9.

HTI RUN CMSL-9

PARAFFINS-WHOLE SAMPLES

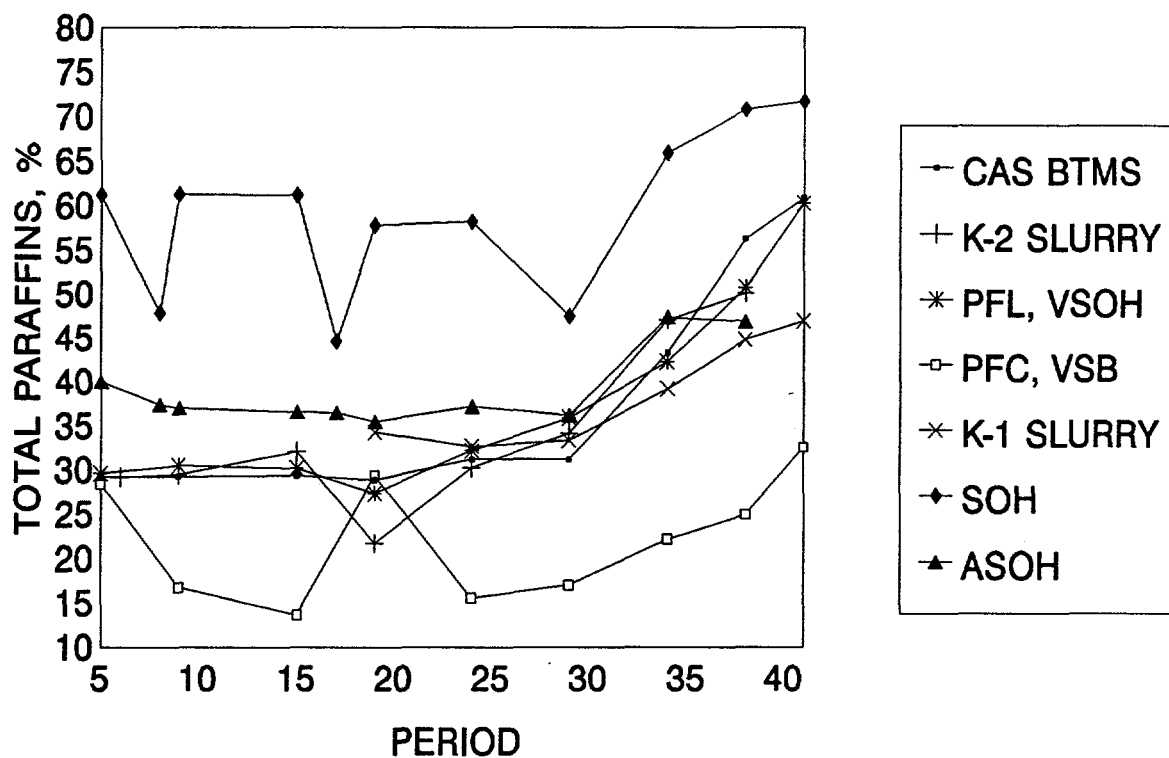


Figure 5. Proton Paraffinicity of Whole Process Stream Samples During HTI Run CMSL-9.

HTI RUN CMSL-9

CAS BTMS - PARAFFINS

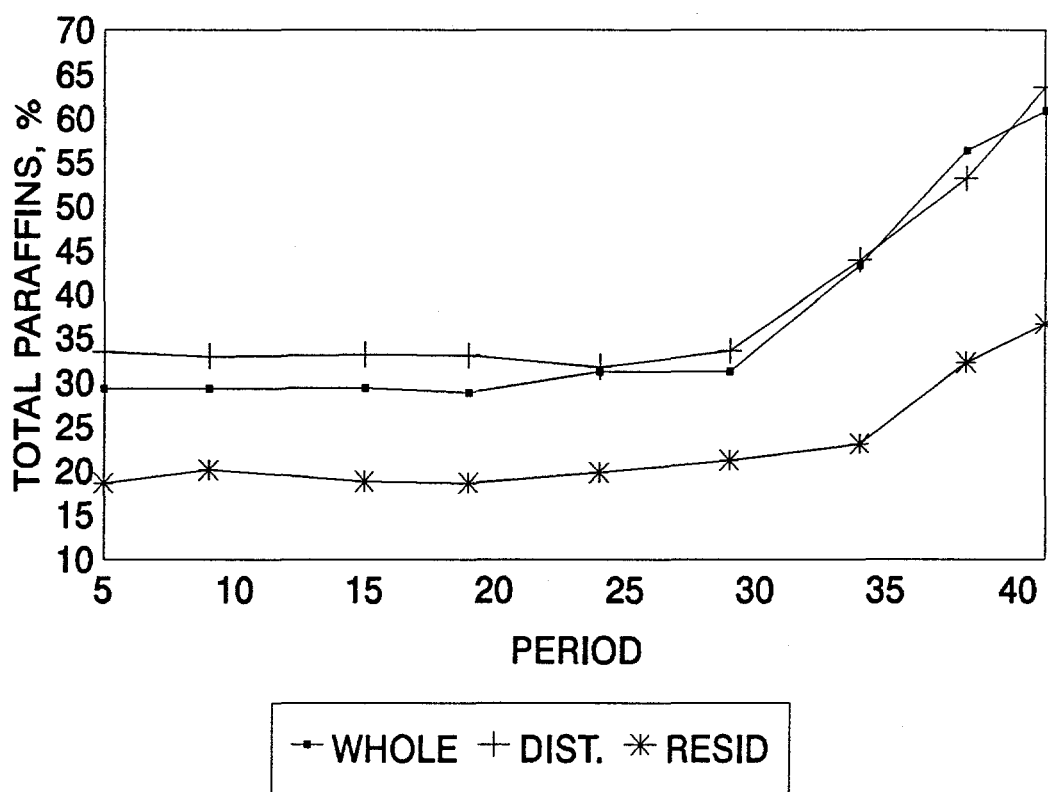


Figure 6. Proton Paraffinicity of Whole CAS Bottoms CAS Bottoms Distillate, and CAS Bottoms Resid Samples During HTI Run CMSL-9.

HTI RUN CMSL-9

CAS BTMS- SOLUBILITY FRACTIONS

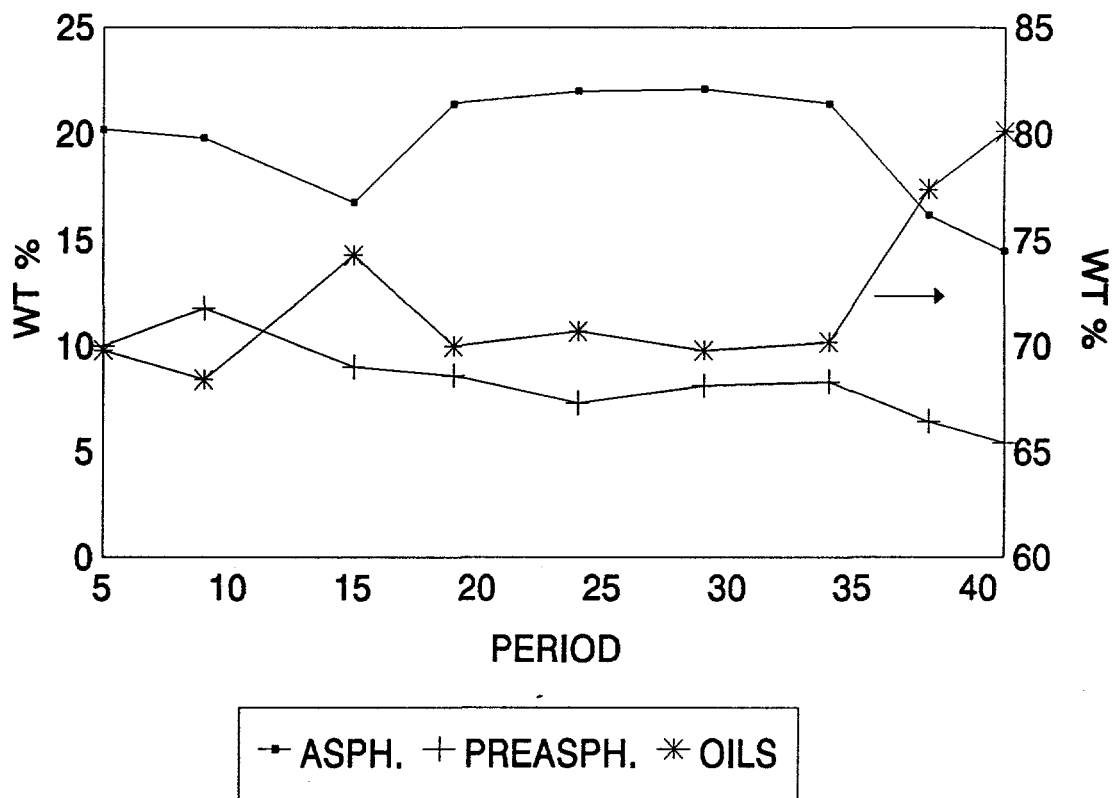


Figure 7. Oil, Asphaltene, and Preasphaltene Content of THF Extracts from CAS Bottoms Resid Samples.

HTI RUN CMSL-9

MICROAUTOCLAVE CONVERSION-DISTILLATES

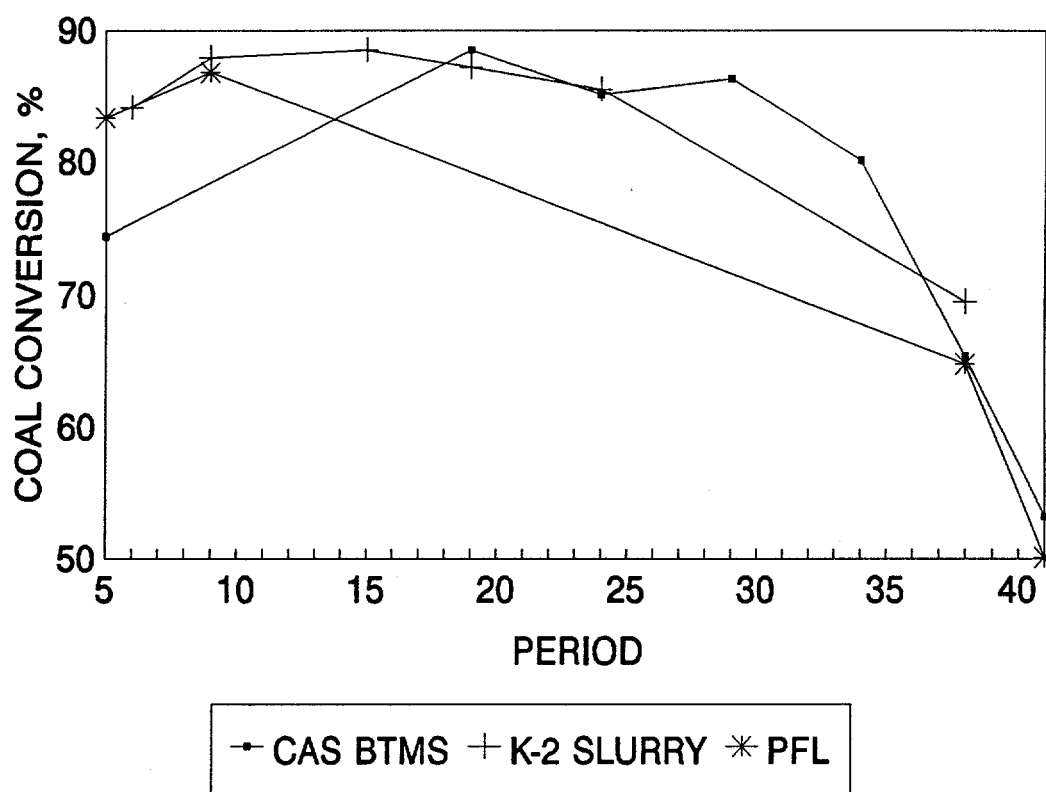


Figure 8. Donor Solvent Quality of Sample Distillates
During HTI Run CMSL-9.

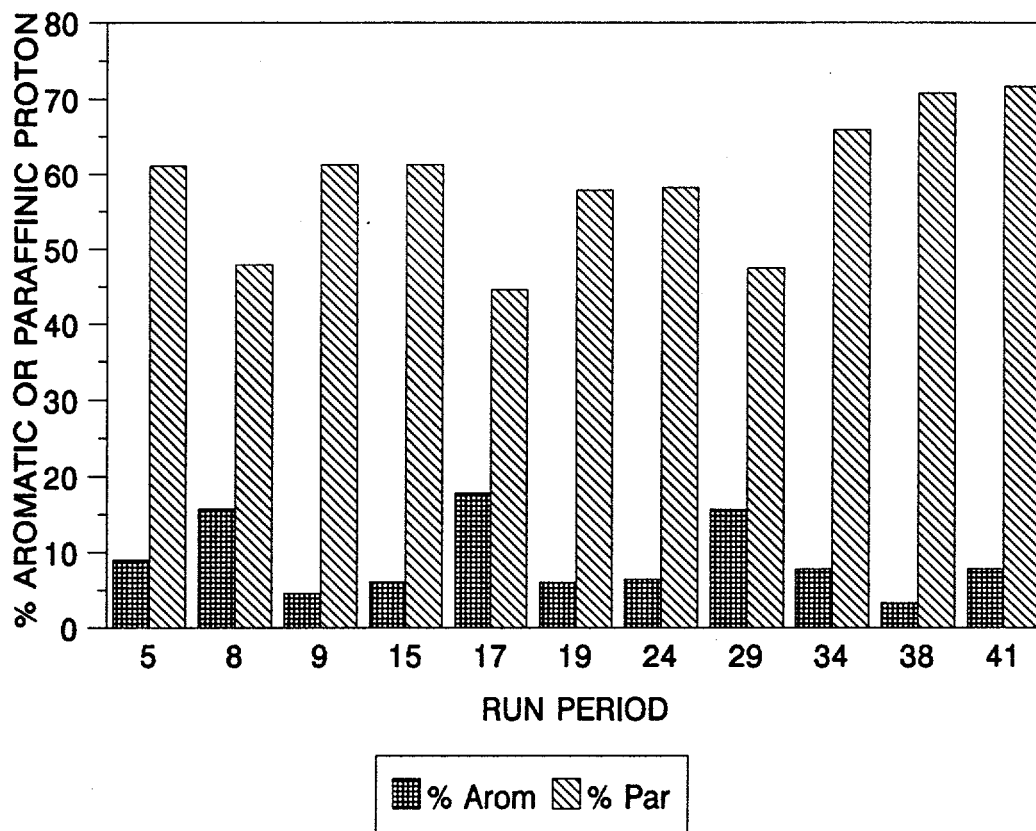


Figure 9. Characteristics of SOH Samples from HTI Run CMSL-9.

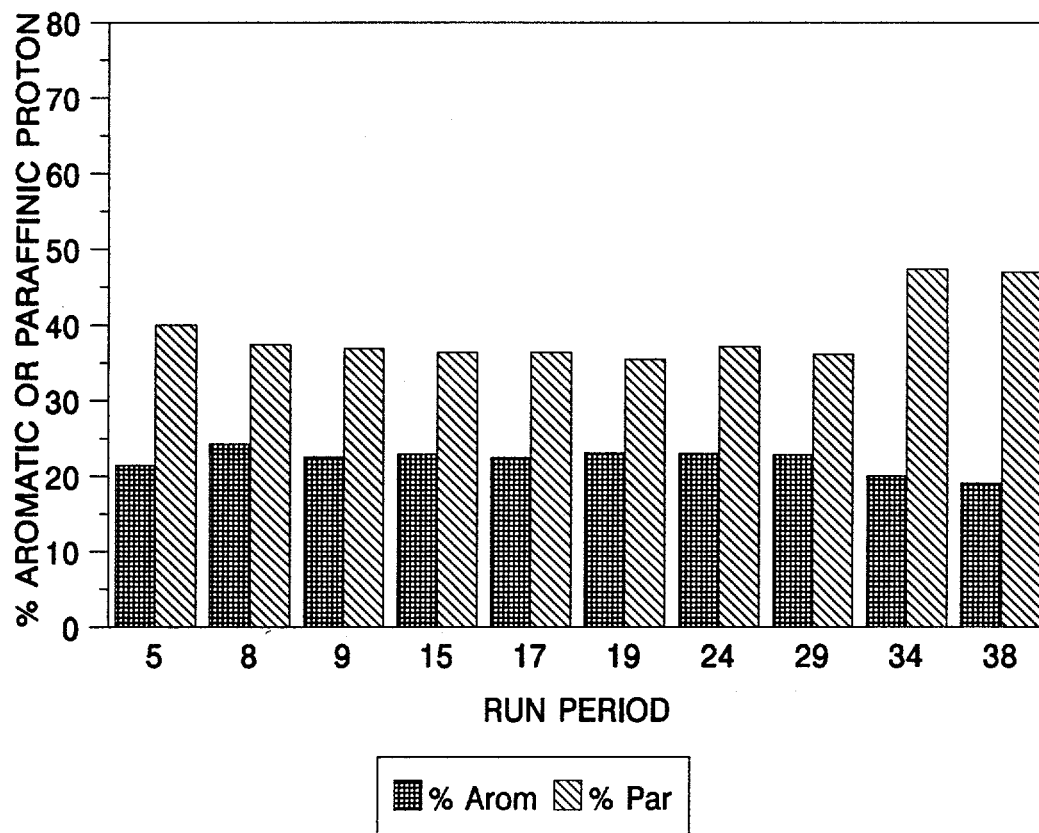


Figure 10. Characteristics of ASOH Samples from HTI Run CMSL-9.

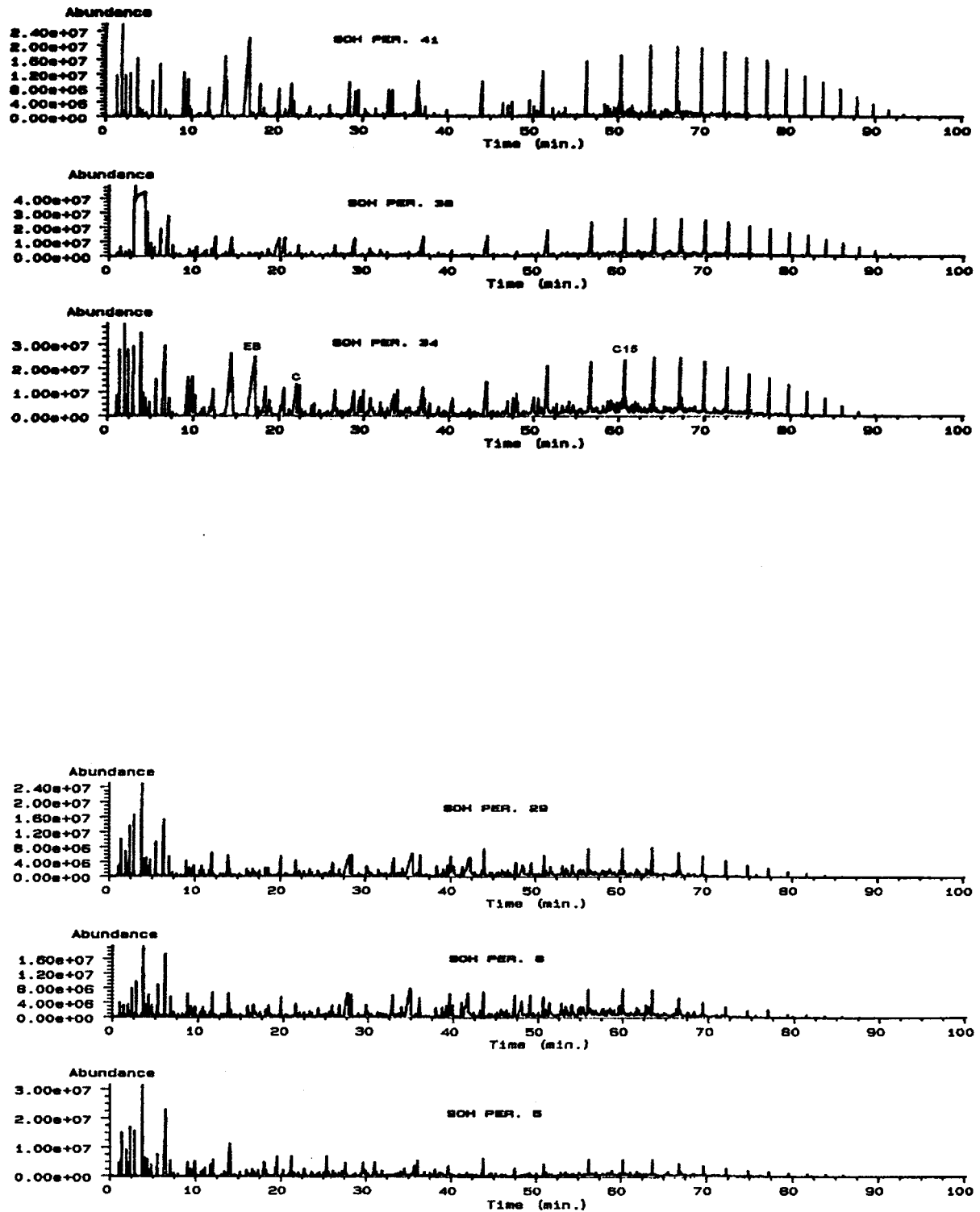


Figure 11. Gas Chromatography-Mass Spectrometry (GC-MS) Total Ion Chromatograms of Selected SOH Samples from Run CMSL-9.

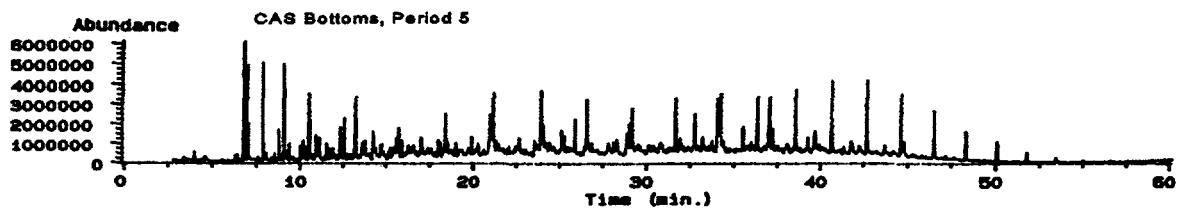
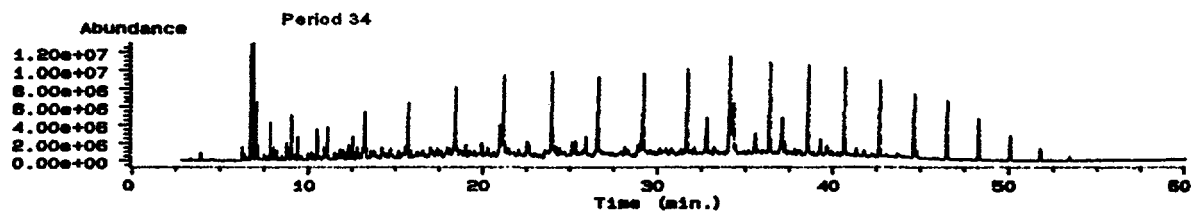
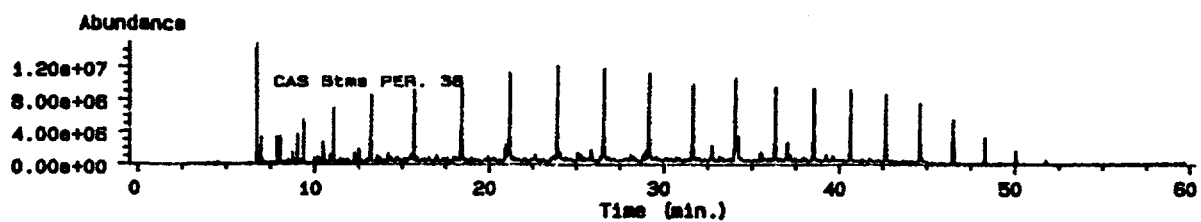
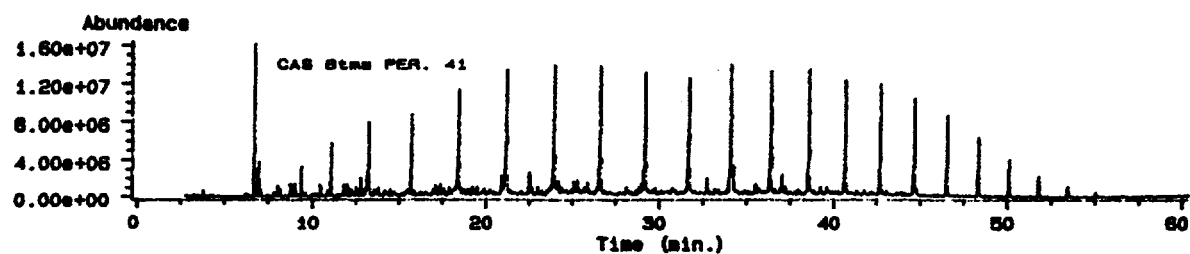


Figure 12. Gas Chromatography-Mass Spectrometry (GC-MS) Total Ion Chromatograms of Selected CAS Bottoms Distillate Samples from Run CMSL-9.

Appendix 1

CHARACTERIZATION OF RUN CMSL-9 SOH SEDIMENT SAMPLES

Observations from Characterization of SOH Sediments

Period 5

FTIR Results

very noisy, generally low intensity
aliphatic CH distinct, OH and Aromatic CH evident
band at 1000 cm⁻¹, small one seems to be at 650 cm⁻¹

Microscopy

blackish (dark gray) overall deposit
red-brown microcrystalline particles, colorless crystals, odd fibers and crystals
edge of filter has appearance of heat-treatment/thin-film interference

Period 8

FTIR Results

1 spectrum good, 1 has distortions
noisy but features good
no band at ca. 1000 cm⁻¹, nothing at 650 cm⁻¹
has narrower OH peak

Microscopy

splotchy thin microcrystalline layer, odd crystals and particles
brown overall deposit

Period 9

FTIR Results

extremely noisy and low intensity
generally featureless bands in general regions as per other samples
1000 cm⁻¹ band indicated, 650 cm⁻¹ band possible

Microscopy

splotchy: overall dark gray, reddish splotches
ca. black microcrystalline particles
mostly thin layer, particles (as above), very few colorless crystals or odd crystals

Period 15

FTIR Results

very distorted U shape
virtually no information available
aliphatic CH only distinct feature

Microscopy

very uniform overall gray appearance
few particles of any kind (some which may be fiber)
edge has heat-treatment/thin-film appearance (see Period 5 description)

Period 19

FTIR Results

generally low intensity

unlike others, region below 2000 cm^{-1} dominant

1000 cm^{-1} peak dominant (except for 400 to 650 cm^{-1})

other regions as in other spectra

Microscopy

overall brownish or brownish-gray appearance

edge has heat-treatment/thin-film appearance

lots of particles, fibers, crystals

Period 24

FTIR Results

very different in overall appearance - 2800 to 3400 cm^{-1} region distorted due to intensity

peaks in 1500 to 600 cm^{-1} region are intense and very sharp

some of these are similar to those in POC-2 sample spectrum and in the other samples

Microscopy

brown overall appearance

thick layer of fine particles

a number of fibers, maybe some colorless crystals

Period 29

FTIR Results

1000 cm^{-1} peak is more dominant here

Microscopy

dark brown to gray mottled appearance

dark gray layer and many small brown particles, other crystals and particles on top

edge has some heat-treatment/thin-film appearance

Period 34

FTIR Results

somewhat narrower OH peak

sharp peak at ca. 630 to 650 cm^{-1} that not all spectra have

Microscopy

light and splotchy in center, brown ring of clumped particles (brown rounded particles and colorless crystals and/or fibers)

Period 38

FTIR Results

coal-like in appearance except that no inorganic features seen

generally good spectrum for overall features

OH, aromatic CH, aliphatic CH, carbonyl, maybe C-O are all evident
somewhat weak 650 cm⁻¹ peak

Microscopy

light brown deposit in center, brown ring of clumped small particles - some black (a few), most brown, some fibers and maybe colorless crystals

Period 41

FTIR Results

broad featureless bands in regions where most of the features are typically seen
presence of OH, aromatic CH, aliphatic CH, carbonyl, and perhaps C-O are all indicated

very weak 650 cm⁻¹ peak

Microscopy

very light overall deposit

mostly isolated particles - fibers, brown particles, maybe a few crystals

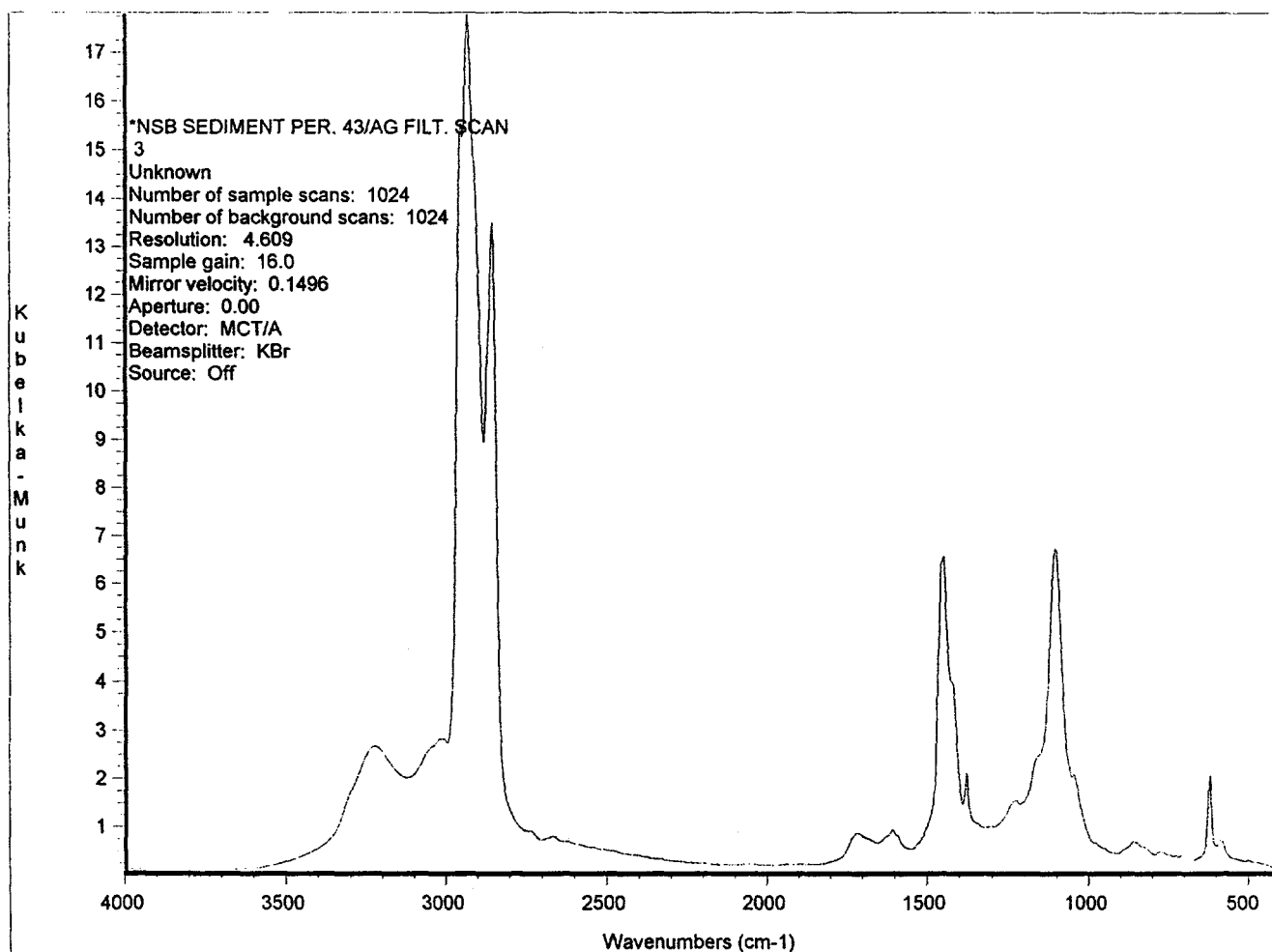


Figure 1-1. Reference FTIR Spectrum of NSB Sediment from Run POC-2, Period 43.

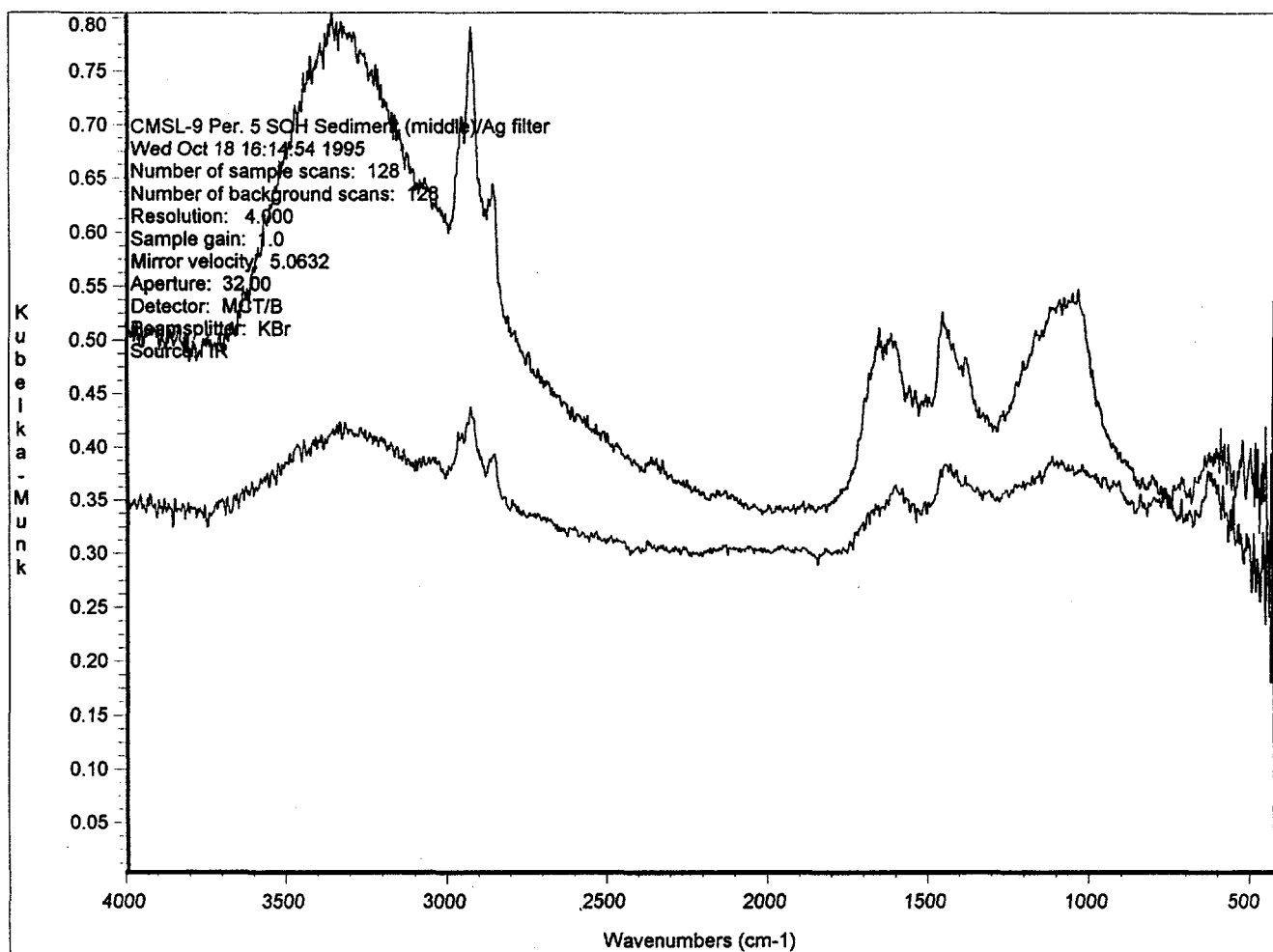


Figure 1-2. FTIR Spectrum of SOH Sediment from Run CMSL-9, Period 5.

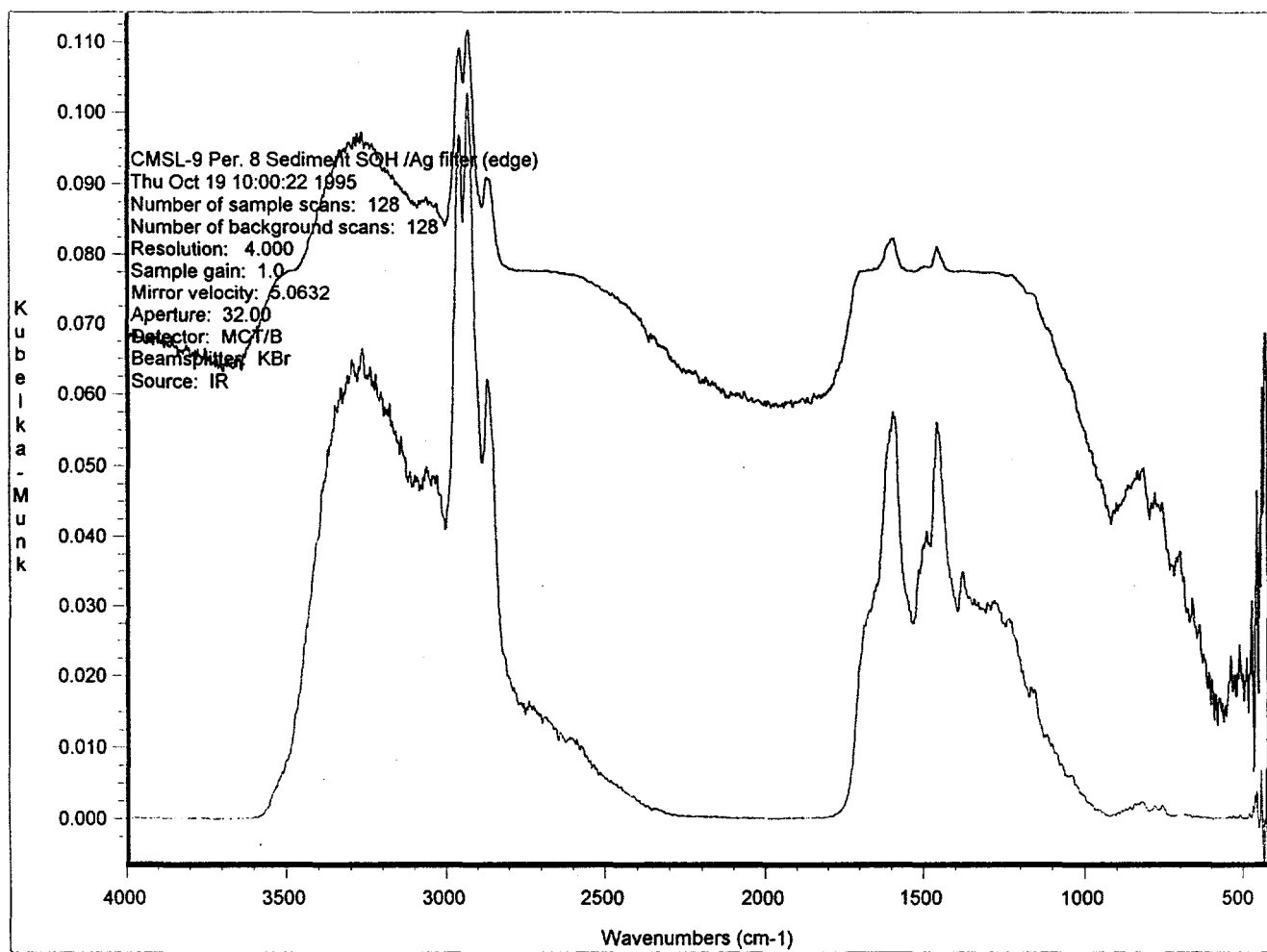


Figure 1-3. FTIR Spectrum of SOH Sediment from Run CMSL-9, Period 8.

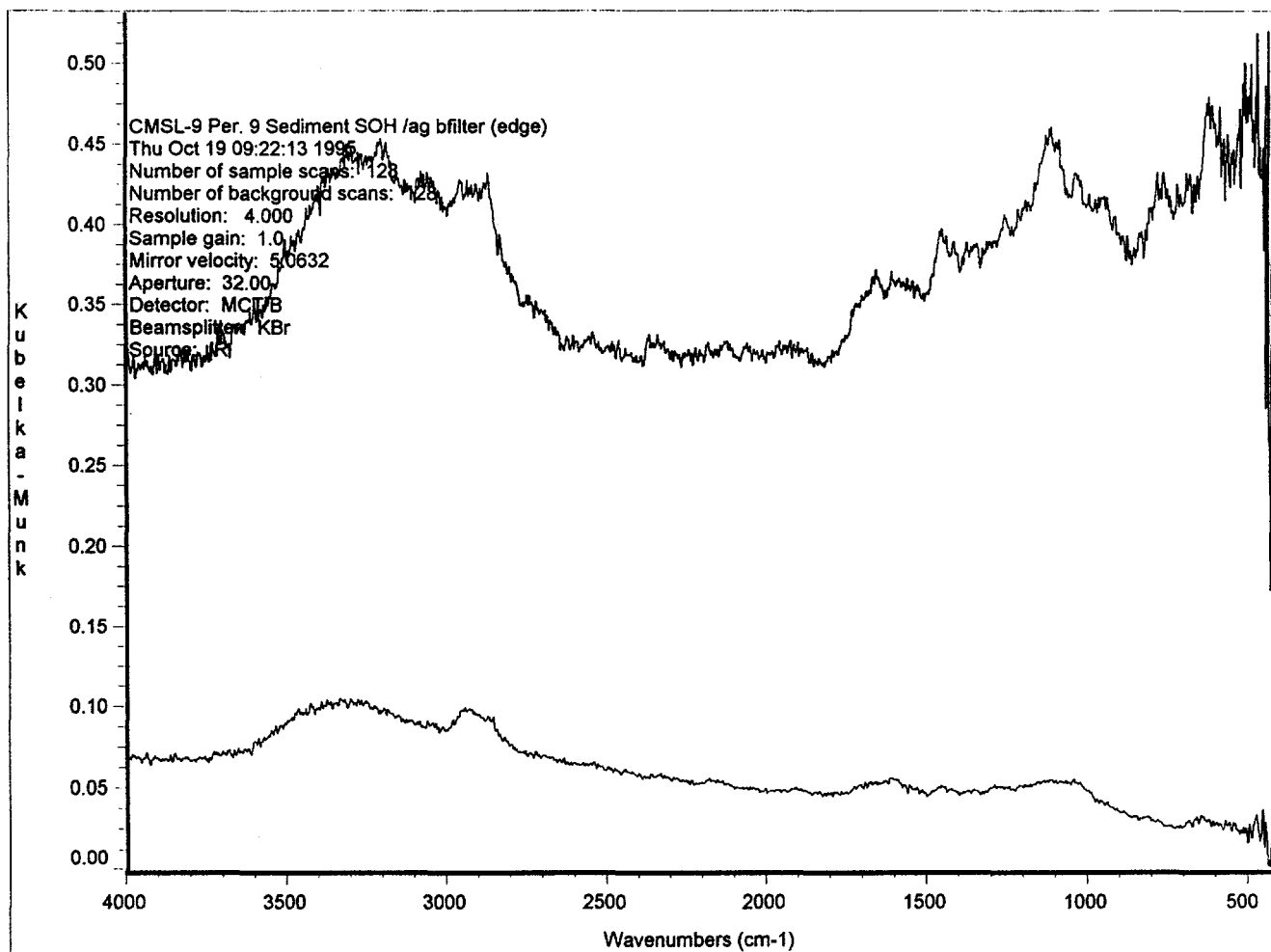


Figure 1-4. FTIR Spectrum of SOH Sediment from Run CMSL-9, Period 9.

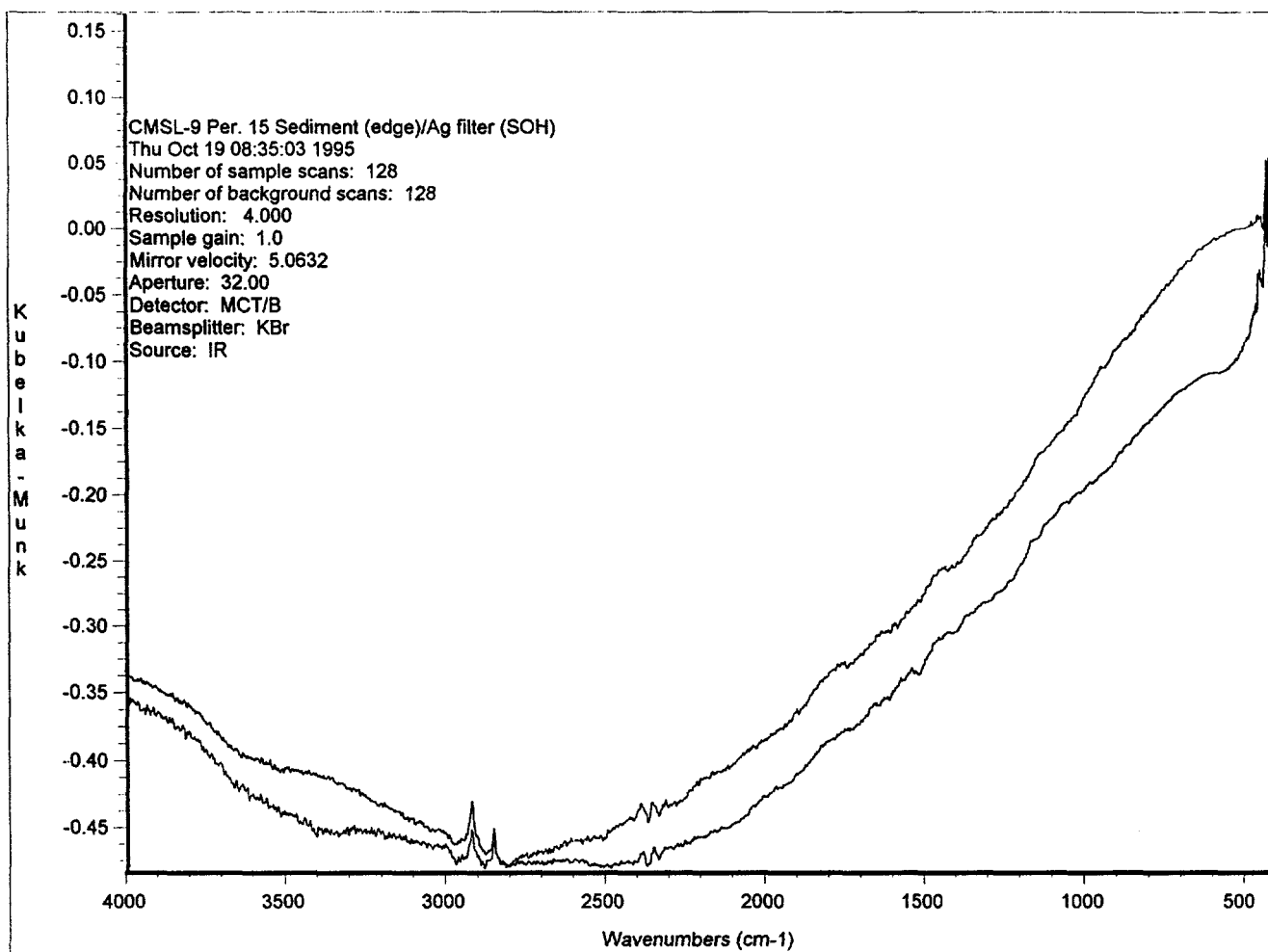


Figure 1-5. FTIR Spectrum of SOH Sediment from
Run CMSL-9, Period 15.

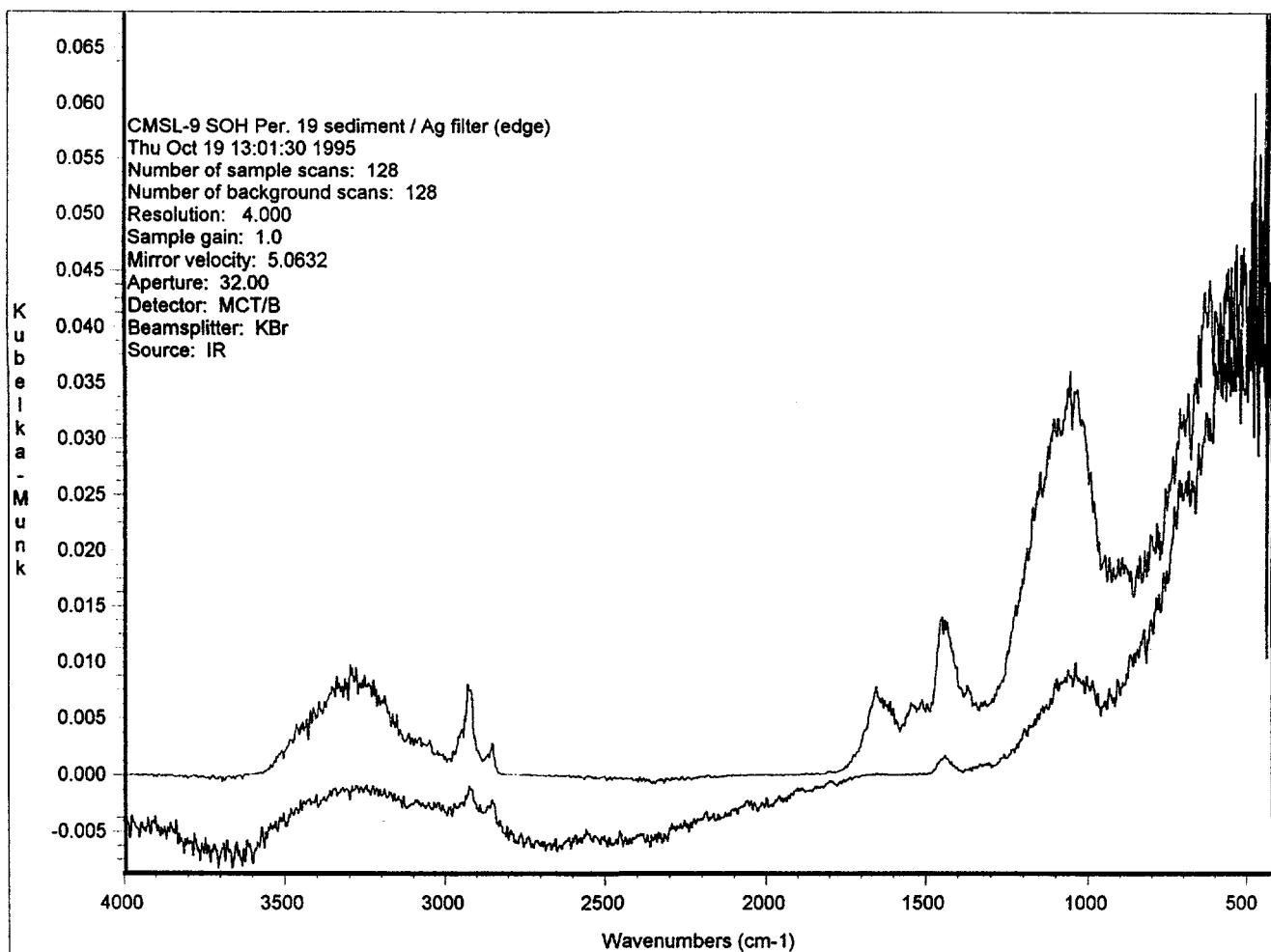


Figure 1-6. FTIR Spectrum of SOH Sediment from
Run CMSL-9, Period 19.

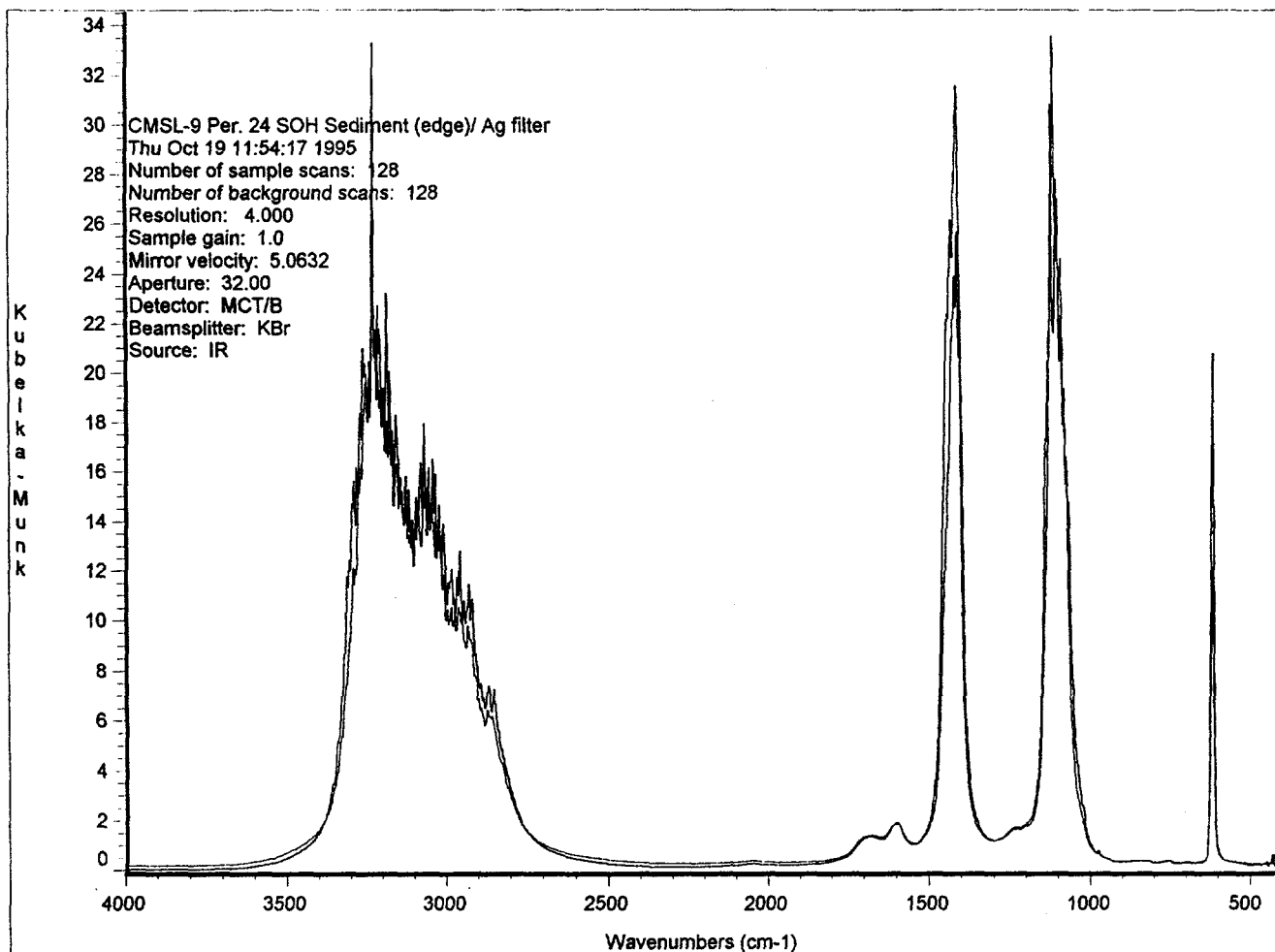


Figure 1-7. FTIR Spectrum of SOH Sediment from Run CMSL-9, Period 24.

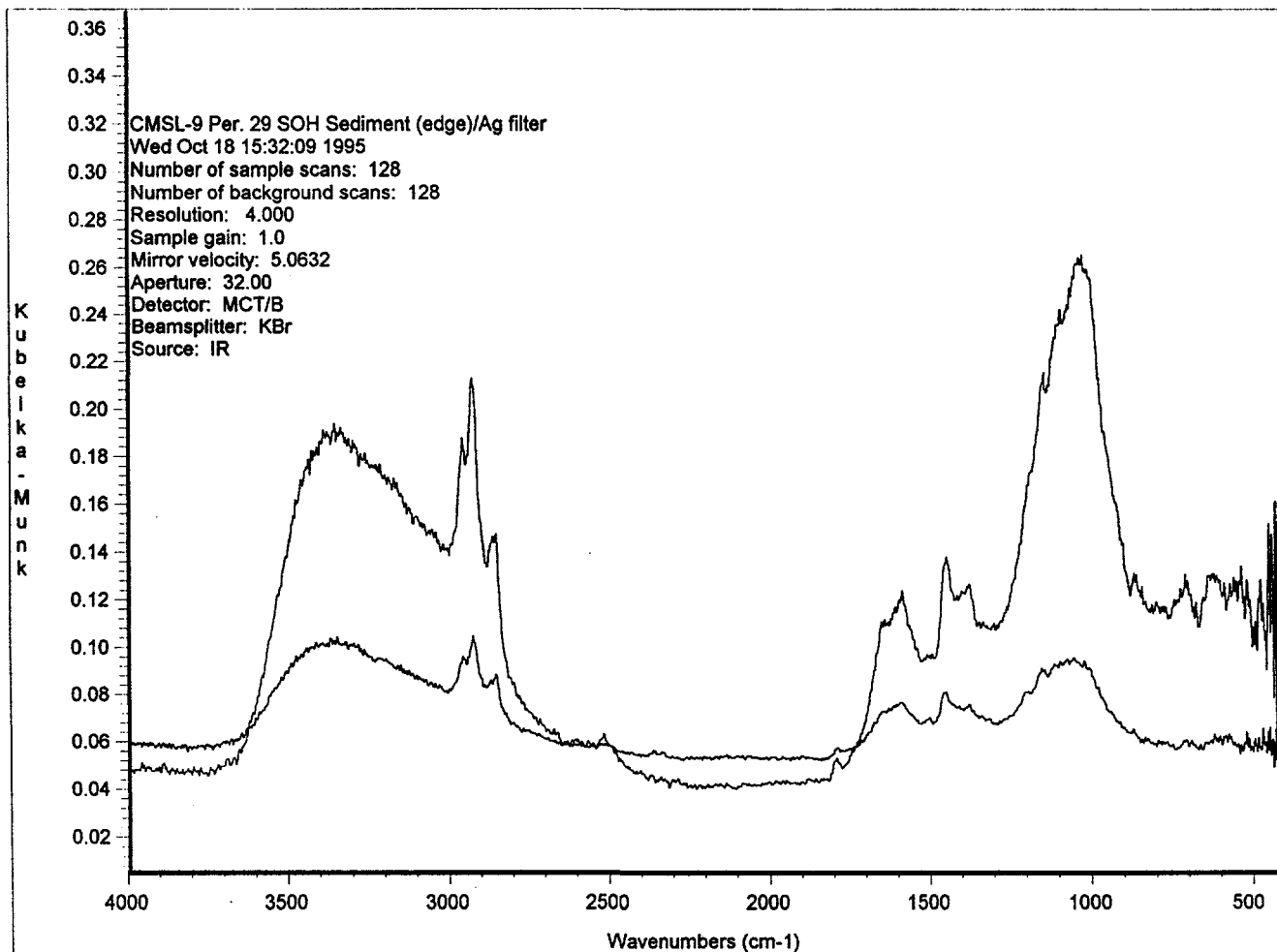


Figure 1-8. FTIR Spectrum of SOH Sediment from
Run CMSL-9, Period 29.

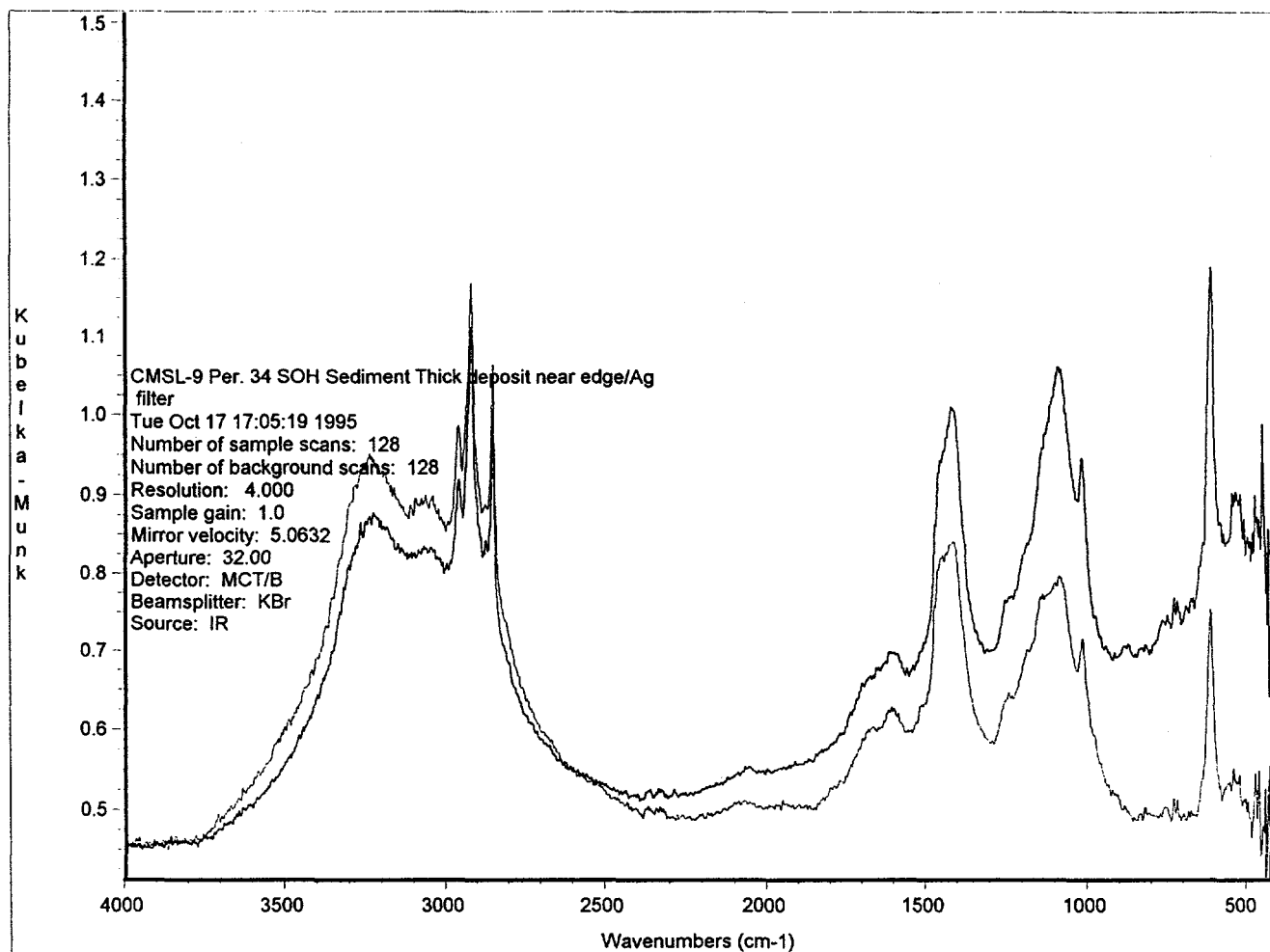


Figure 1-9. FTIR Spectrum of SOH Sediment from Run CMSL-9, Period 34.

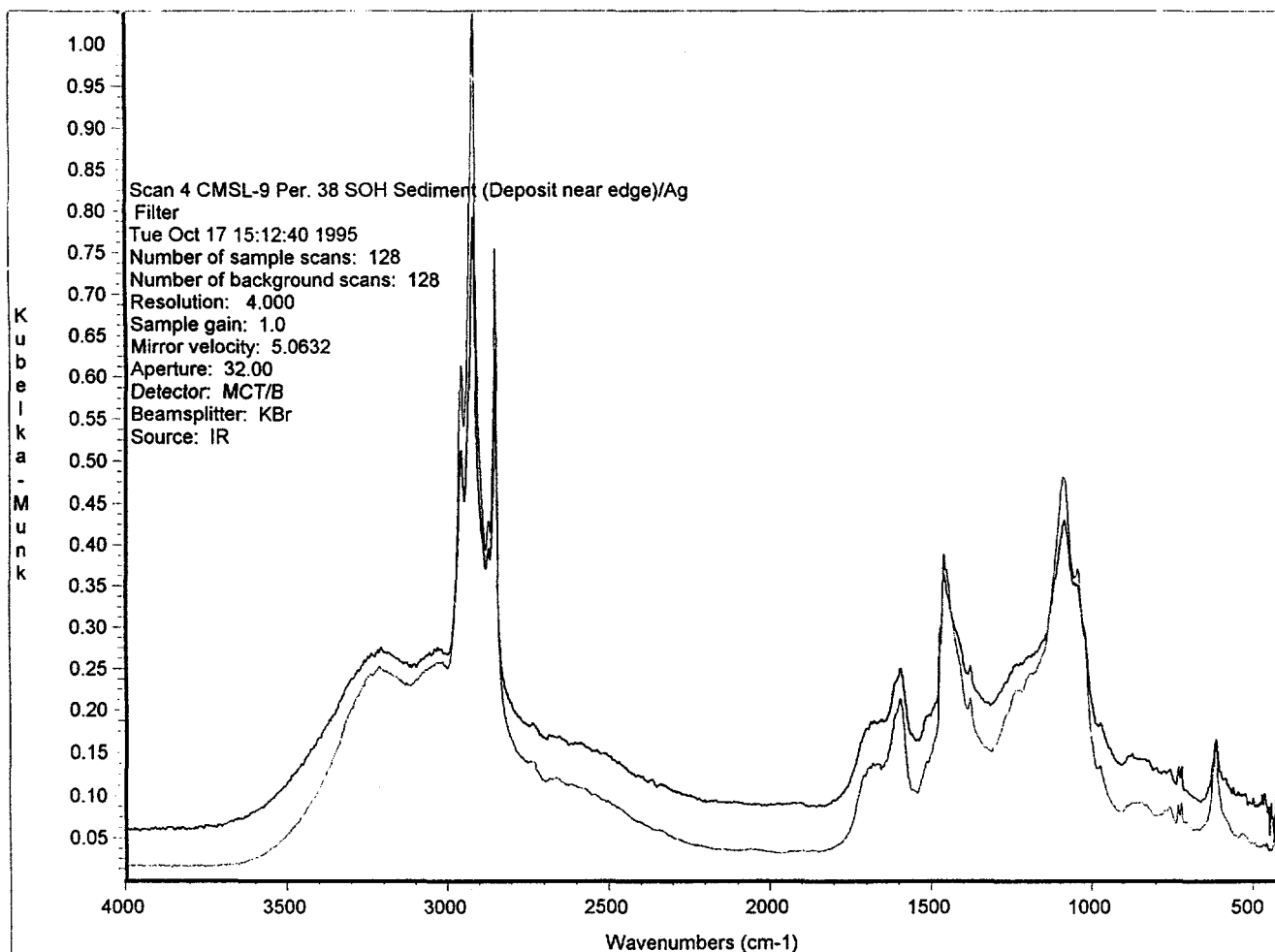


Figure 1-10. FTIR Spectrum of SOH Sediment from Run CMSL-9, Period 38.

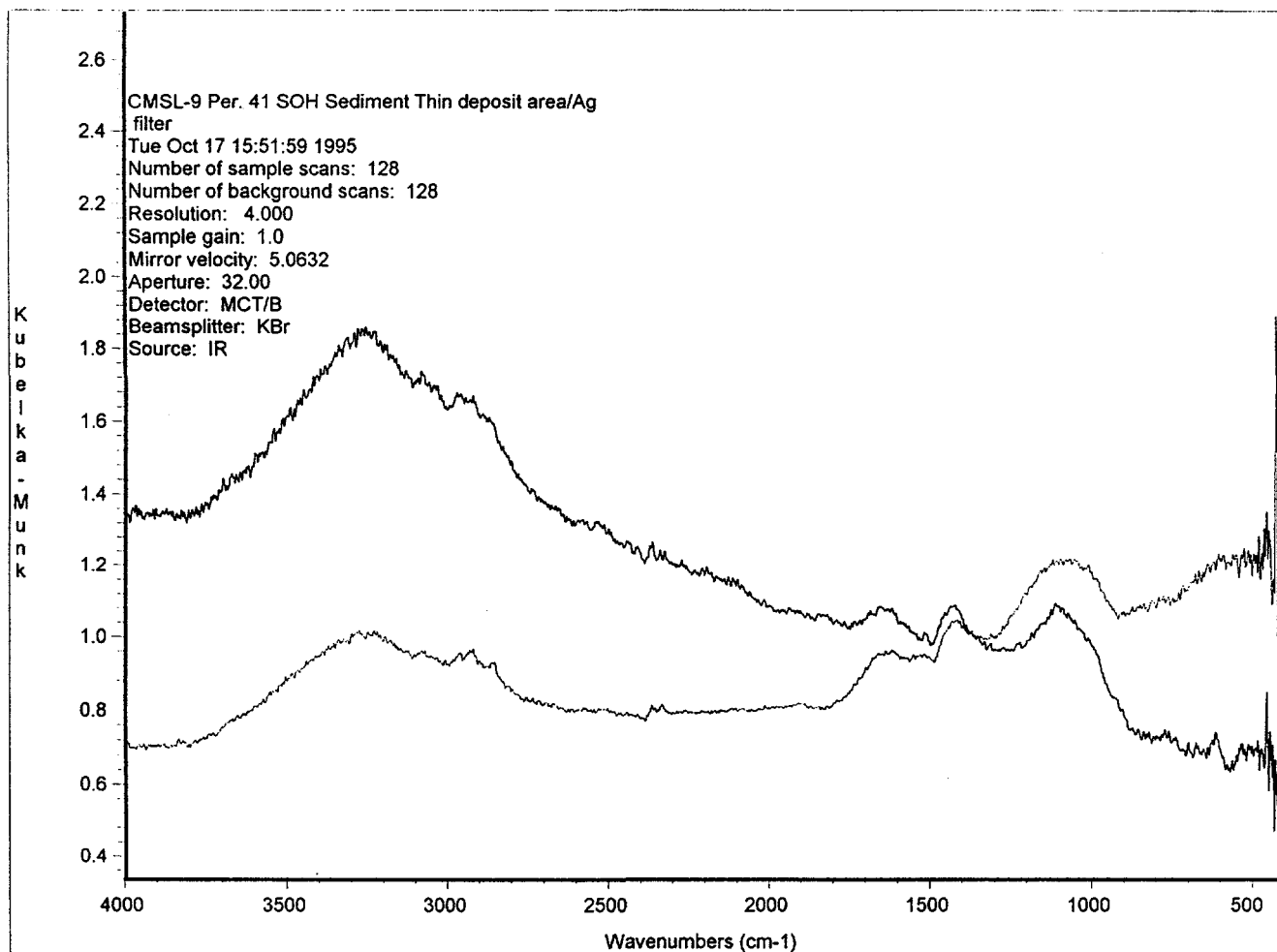


Figure 1-11. FTIR Spectrum of SOH Sediment from Run CMSL-9, Period 41.

Appendix 2

SAMPLE REQUEST - RUN PB-02



CONSOL Inc.
Research & Development
4000 Brownsville Road
Library, PA 15129-9566
412-854-6600
FAX: 412-854-6613
412-854-6748

November 13, 1995

Dr. V. Pradhan
Hydrocarbon Technologies, Inc.
P.O. Box 6047
New York and Puritan Avenues
Lawrenceville, NJ 08648

Dear Vivek:

Our sample request for POC Bench Option Run 2 is described below. We are requesting material in sufficient quantities to allow for sample distribution to other research groups, as needed. We understand that you cannot always provide the requested amounts, and we can work with smaller quantities.

We would like to receive from each run condition: (1) 250 g of separator overhead (SOH) and 250 g of atmospheric still overhead (ASOH) or 250 g of SOH/ASOH blended in the correct product ratio; (2) 350 g of pressure-filter liquid (PFL); (3) 350 g of pressure-filter cake (PFC); (4) 350 g of continuous atmospheric still (CAS) bottoms; and (5) 350 g of interstage sample (first-stage product). Please also include: (6) 350 g of the start-up/make-up oil; (7) 250 g samples of SOH and ASOH liquids from any bypass periods of the in-line hydrotreater; (8) a fresh 300 g sample of each of the coal and petroleum resid feeds; and (9) 1 kg of the plastic feed.

Let us know of any problem areas with this request. Thank you for your assistance.

Sincerely,

G. A. Robbins
Sr. Research Chemist

GAR:ls

cc: A. G. Comolli - HTI
M. A. Nowak - PETC
E. B. Klunder - PETC
F. P. Burke
R. A. Winschel
S. D. Brandes

Appendix 3

UNIVERSITY OF DELAWARE QUARTERLY REPORT

**THE KINETICS OF COAL LIQUEFACTION DISTILLATION
RESID CONVERSION**

**QUARTERLY REPORT
10/16/95-1/15/96**

**Michael T. Klein
Principal Investigator**

**William H. Calkins
Co-Principal Investigator**

**He Huang
Research Associate**

and

**Shaojie Wang
Visiting Scientist**

**Center for Catalytic Science and Technology
Department of Chemical Engineering
University of Delaware
Newark, Delaware 19716**

**Date Published
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EXECUTIVE SUMMARY

An alternative method of determination of conversion of resid hydroprocessing is being tested which may shorten the work-up procedure. Results of these tests will be compared with the established method.

Three hydroprocessing runs of resid carried out by CONSOL in small shaker bombs are designed to provide a preliminary basis for selection of catalyst type to be used and to compare with runs made in the SCTBR apparatus.

Molecular weights have been determined for a number of Sara fractions to provide the data for modelling. An effort is being made to apply the SimDis TGA method to resids to obtain their boiling point distribution for modelling purposes.

A TG/MS analytical system is been installed for determining the molecular species produced in the resid hydroprocessing.

QUARTERLY REPORT

ANALYTICAL DEVELOPMENT

To determine the conversion in tetralin of resid in the presence of hydrogenation catalyst, it has been necessary to determine the amount of low boiling products (below 850°F) formed. Up to now we have been separating the solids in the hydroprocessing products by filtration, washing the solids on the filter with fresh solvent and determining the percent conversion on the solids by ash content determined by TGA. The boiling range of the liquid has been determined by the recently developed SimDis TGA procedure (1). This allowed us to determine the conversion as the product of the conversion to liquid and the fraction of liquid boiling below 850 °F. This calculation assumed the solid and liquid samples were representative aliquots. The method was shown to be reproducible but quite time consuming and had the disadvantage of cumulative errors in the separate determinations.

An alternative method of determination of conversion suggested by CONSOL is to take the weight of the solid filter cake without extensive washing, determine the material boiling above 850°F (and therefore the percent boiling below 850°F) on both the solid and the liquid and force a material balance based on the organic content of the original resid charged to the reactor. This approach is being tested for comparison with our established procedure. However we have encountered a problem with the SimDis TGA on the solid sample. The quartz pans we have been using are not easy to charge with the solid sample, and it is almost impossible to remove the ash from the SimDis TGA pan. The special metal pans we have, with a laser-punched hole at the top, hold too little sample for adequate precision and have other problems. We have ordered some larger pans with laser punched holes at the top, and will test them when they are received. In the meantime we have shown that we can determine the fraction of solid and the residual liquid in the solid boiling above 850°F (but not the boiling range) adequately with the conventional open pans using the ramp method, and are proceeding to do so.

For calculating the conversions, the mass balance in each hydroprocessing run gives,

$$m_p = m_c + m_{lost} + m_{gas} \quad (1)$$

where m_p is the mass of the products; m_c is the mass of the condensed material, i.e. residue solid and liquid; m_{lost} is the mass of the lost material; and m_{gas} is the mass of the gas products. The condensed material was filtered into solid residue and liquid filtrate without the use of solvent wash and the solid cake and liquid filtrate were weighed and recorded as m_{solid} (the mass of the solid residue) and m_{liquid} (the mass of the liquid filtrate). The fraction of the liquid filtrate boiling above 850 °F, $f_{liquid,850°F+}$ (or below 850 °F) is determined by the SimDis TGA method (1). The fraction of the solid residue boiling above 850 °F, $f_{solid,850°F+}$ (or below 850 °F) is determined by a modified SimDis TGA method. If m_{lost} is considered, as discussed above, to be high-boiling material (i.e., boiling at temperature higher than 850 °F), the mass of the hydroprocessed products boiling above 850 °F is:

$$m(850^{\circ}F^{+}) = m_{lost} + f_{liquid, 850^{\circ}F^{+}} \times m_{liquid} + f_{solid, 850^{\circ}F^{+}} \times m_{solid} \quad (2)$$

Therefore, conversion of the resid to 850 °F in hydroprocessing is estimated by:

$$Conversion(850^{\circ}F^{+}) = 1 - \frac{m(850^{\circ}F^{+})}{resid\ charged} \quad (3)$$

When a catalyst is used in the resid hydroprocessing, a blank SimDis TGA is run on this catalyst for any correction.

At the same time, we have the problem of selection of the catalyst for testing convertability of the resids we plan to test in the project. The sulfided molybdenum naphthenate appears to work and does not create a significant error in the ash determination for conversion calculation. However, there are significant advantages in using the Shell 324 heterogeneous catalyst that has been used in the pilot plants. The high ash content of that catalyst and the high concentration in which it is used creates too much of an error in conversion calculation in our SCTBR reactor which depends on aliquots. CONSOL has therefore prepared three shaker bomb runs, one with no catalyst, one with sulfided molybdenum naphthenate, and one with the Shell heterogeneous catalyst. We are working up these runs by the alternative method described above, using the open pans. There was about a 10% loss of material in these runs which is not too different from the recovery we are getting in the SCTBR runs, however, we hope these tests will provide a test of the work-up methods and give us a basis for deciding what catalyst we wish to use in the evaluation of the convertability of the resid samples.

A series of hydrotreating runs with and without sulfided molybdenum naphthenate catalyst showed quite good reproducibility by the established method (Table 1). However, the presence of even 0.9 wt% of Mo catalyst based on the charged resid showed only minor increase (<1% conversion difference) over the uncatalyzed reaction. Whether this is due to some catalytic material already in the resid, poisoning of the catalyst by some species in the resid, and/or low reactivity of the resid itself remains unknown. For that reason, we have made several hydroprocessing runs of resid using various concentrations of sulfided molybdenum naphthenate catalyst, ranging from 1 to 5 wt% of Mo based on the resid charged. While there is considerable scatter in these data, it is clear that the sulfided molybdenum naphthenate catalyst with 5 wt% of Mo-catalyst at 430 °C is quite active.

MODELLING

To date, molecular weights have been determined for each of the aromatic fractions and several of the resin and asphaltene fractions. Saturate MWs will be the next fractions which will be measured. Dichlorobenzene is used for the aromatics, resins, and asphaltene fractions. Toluene is used for the saturate fractions and initially THF or pyridine is used for the pre-asphaltene fractions. Determination of a few fractions for Saturates should take approximately

two weeks. The analytical results acquired so far are given in Table 2. The time required to determine the pre-asphaltene molecular weights will depend on selecting an appropriate solvent.

All other analytical results have been obtained with the exception of SimDis results on the resids. We will attempt to use the developed SimDis TGA method to obtain these results with the modification of using the large metal pans with the laser punched hole at the top. In the mean time, once molecular weights are determined for a few saturate and asphaltene fractions, initial molecular constructions will be assembled without SimDis information. The VPO measurements should give fairly good estimates of average molecular sizes so that lack of SimDis information may not be too critical. Furthermore, more NMR data has been supplied than is typical. This information should further help determine a unique set of molecular attribute pdf's.

At this point it is probably not advantageous to try to obtain any more analytical information (e.g. analytical pyrolysis). Such information yielded little extra insight into the structures for petroleum resid, and is likely to be useful only if the initial resid analytical information is not adequate to sufficiently narrow the parameters of the molecular attribute pdf's. The molecular construction algorithm is pretty well established at this point so that the limiting factor now is obtaining the last bits of analytical information.

TG/MS ANALYSIS OF RESID AND RESID CRACKING PRODUCTS

A Netzsch Thermogravimetric Analyzer together with a special temperature controlled transfer line has now been received. We plan to use it in conjunction with a high resolution mass spectrometer in the Chemistry Department to investigate the composition of the resid hydroconversion products in order to obtain information about the chemical composition of these materials and how they vary from resid to resid. When first received it was apparent that the instrument was too sensitive to vibration to be mounted in the usual way by the mass spectrometer. Considerable effort was expended to eliminate the vibration in that location. However, by mounting the instrument on a heavy stone slab which was placed on thick rubber sheets, the instrument now appears to be essentially vibration-free. We are now cooperating with the Chemistry Department in testing the transfer line from the TGA into the mass spectrometer.

Table I Resid Conversion

Name	T C	t min	Catalyst	SA g	Gas	Ash (TGA) wt%	TSF wt%	RSF in Tetralin wt%	850 F+ in Tetralin wt%	Conversion wt%
C047	435	30	Mo-naph.	1	H2	56.4%	71.3%	13.4%	10.2%	16.9%
C048	435	30	Mo-naph.	1	H2	54.4%	70.2%	12.7%	9.9%	15.3%
C049	436	30	Mo-naph.	1	H2	56.3%	71.2%	12.6%	9.7%	16.5%
C050	436	30	Mo-naph.	1	H2	56.5%	71.4%	12.8%	9.9%	15.9%
C051	437	30	Mo-naph.	1	H2	55.4%	70.8%	12.6%	9.7%	15.9%
				Mean		55.8%	71.0%	12.8%	9.9%	16.1%
				Std		0.8%	0.4%	0.3%	0.2%	0.5%
C052	437	30			H2	50.4%	67.9%	10.8%	8.3%	15.7%
C053	436	30			H2	50.4%	67.9%	10.7%	8.3%	15.4%
C054	436	30			H2	50.6%	68.0%	11.2%	8.5%	16.5%
C055	437	30			H2	50.8%	68.2%	10.5%	8.3%	14.6%
C056	436	30			H2	50.4%	67.9%	11.8%	8.9%	16.3%
				Mean		50.5%	68.0%	11.0%	8.5%	15.7%
				Std		0.2%	0.1%	0.5%	0.3%	0.7%

Table 2: VPO results

Sample Number	Saturate MW	Aromatic M W	Resin MW	Asphaltene M W	Pre-Asphaltene M W
1		320	676	1620	
2		274	613	1533	
3		319	568	1472	
4		362	718	1736	
5		493	789	1827	
6		420			
7		348			
8		425			
9		323			
10		430			
11		386			
12		413			
13		336			
14		356			
15		345			

Appendix 4

UNIVERSITY OF DELAWARE TRIP REPORT

Contract Title and No.: A Characterization and Evaluation of Coal Liquefaction Streams
DE-AC22-94PC93054

Contractor Name and Address: CONSOL Inc.
Research & Development
4000 Brownsville Road
Library, PA 15129

Meeting Location and Date: The University of Delaware, Newark, DE
December 11, 1995

Participants:

CONSOL

F. P. Burke
R. A. Winschel
S. D. Brandes

University of Delaware

W. H. Calkins
M. T. Klein
H. Huang
S. Wang
D. Campbell

SUMMARY AND ACTION ITEMS

The subject meeting was held at the University of Delaware to review Delaware's progress and to formulate near-term plans for experimental work. Presentations were made by He Huang, and Darin Campbell and Mike Klein. An agenda for the meeting is attached. Handouts are attached to the DOE copy.

The following action items were identified.

1. Delaware will repeat a number of experimental tests in the STBR using molybdenum naphthanate catalyst to determine the reproducibility of resid conversion data using a method based on the weight of the tetralin-insoluble ash-free filter cake plus the weight of the 850 °F⁺ resid in the tetralin solubles and forcing a material balance through an ash balance (Method 1). These data will be compared to the data previously obtained by measuring the amount of 850 °F⁻ material formed in the reaction (Method 2).

$$\text{conversion} = 1 - \frac{B+C}{A} \quad (1)$$

$$\text{conversion} = 1 - \frac{B+C}{B+C+D} \quad (2)$$

A = Mass of ash-free residual feed
B = Mass of ash-free tetralin-insoluble product
C = Mass of 850 °F⁺ tetralin-soluble product
D = Mass of 850 °F⁻ tetralin-soluble product

12. CONSOL will perform three tests in the 45 mL microautoclave using no catalyst, supported Shell 324 catalyst, and the molybdenum naphthanate catalyst. The products of these reactions will be recovered without extraneous solvent and sent to Delaware for work-up. The weight of vented gas and the weight of product left unrecovered in the reactor will be recorded by CONSOL. Run conditions will be the following: 435 °C, 30 min, at least 1500 psi of H₂ at 435 °C, 1:1 wt:wt catalyst to resid for the supported catalyst, 0.9 wt % (of resid) Mo for the molybdenum naphthenate run. The Shell 324 catalyst will be the same presulfided-then-washed catalyst that CONSOL shipped to Delaware. The size of the Shell 324 catalyst (pellets or grind size) used will be agreed to in advance. These results will help us to select the baseline catalyst for future work.
3. Delaware will use the procedure that they have been using to date to work up the microautoclave products produced by CONSOL (i.e., filtration, and two TGA experiments, one to obtain the sim-dist and the other the iso-track method to get the 850 °F[±] fractions).
4. Delaware will not proceed with any runs using supported catalyst until the results of the three CONSOL microautoclave tests are known. However, they will continue to consider ways in which the work could be conducted in the STBR with supported catalysts.
5. Delaware will not pursue the development of a vacuum distillation method to work up products of the STBR.
6. Delaware will complete the molecular weight measurements on the SARA fractions of the fifteen resid samples.
7. CONSOL will send to Darin Campbell copies of analyses of the fifteen resid samples, including elemental analyses, ¹³C-NMR data, ¹H-NMR data, phenolic - OH contents, and SARA separation data.
8. Delaware will use the analytical information supplied to them, and the data they generate, to create molecular representations, optimize the objective functions using as many terms that are considered reliable, and proceed to "test" the quality of the model system by comparing predicted properties to experimentally determined properties.

Appendix 5

DOE-PETC/AIST-NEDO PAPER

CHARACTERISTICS OF PROCESS OILS FROM HTI COAL/PLASTICS CO-LIQUEFACTION RUNS

G. A. Robbins
S. D. Brandes
R. A. Winschel
F. P. Burke



CONSOL Inc.
Research & Development
4000 Brownsville Road
Library, PA 15129

Prepared for Presentation at the
1995 US/Japan Joint Technical Meeting (NEDO)

Sendai, Japan
October 16-19, 1995

CHARACTERISTICS OF PROCESS OILS FROM HTI COAL/PLASTICS CO-LIQUEFACTION RUNS

G. A. Robbins, S. D. Brandes, R. A. Winschel, F. P. Burke

CONSOL Inc.
Research & Development
4000 Brownsville Road
Library, PA 15129

OBJECTIVE:

The objective of this project is to provide timely analytical support to DOE's liquefaction development effort. Specific objectives of the work reported here are:

- to determine the fate of the plastics feedstocks, relative to coal-only operation;
- to determine the conversion of the feedstocks;
- to determine the product streams to which the feedstocks are converted (bottoms vs. distillate);
- to determine interactions of feedstocks;
- to determine how use of plastics feedstocks affect product quality; and
- to determine to what degree property differences reflect feedstock differences vs. other (process) condition changes, such as unit operations, space velocity, and catalyst age.

ACCOMPLISHMENTS AND CONCLUSIONS:

Introduction

During a few operating periods of Run POC-2, HTI co-liquefied mixed plastics with coal, and tire rubber with coal. Although steady-state operation was not achieved during these brief test periods, the results indicated that a liquefaction plant could operate with these waste materials as feedstocks. CONSOL analyzed 65 process stream samples from coal-only and coal/waste portions of the run. Some results obtained from characterization of samples from Run POC-2 coal/plastics operation are:^{1,2}

1. Polystyrene (PS) products were identified and quantified in distillate product oil.
2. Incompletely converted high-density polyethylene (HDPE) was found as tetrahydrofuran (THF)-insoluble material in the ash-free-resid recycle stream. It was unclear to what extent this material was present in the ROSE bottoms stream. Unusual solubility behavior seems to be associated with HDPE-derived material in resid-containing streams. The broad implication is that HDPE was not completely converted in the liquefaction process.
3. The unusual presence of a product-oil sediment raised questions about the stability of the product oil.
5. Analytical issues were identified including how to identify and quantify HDPE, the appropriateness of coal liquefaction work-up procedures to

coal/plastics liquefaction, and how to measure the extent of plastics liquefaction.

Along with the analytical difficulties, the brevity of the coal/plastics liquefaction period in Run POC-2 prevented these issues from being resolved. To better evaluate these issues, Run CMSL-8 was performed at a smaller scale and over a longer period than Run POC-2. There were other differences too, such as reactor and temperature configuration and the feed coal used. However, the plant operated in solvent balance, which did not occur during the coal/plastics portion of Run POC-2. Solvent-balanced operation in Run CMSL-8 meant that samples, material balances, and performance results from Run CMSL-8 were representative of operation with the coal/plastics feedstocks. Coal/HDPE liquefaction was tested in Run CMSL-8, in addition to coal/mixed plastics liquefaction. The background and results from characterization of Run CMSL-8 process oil samples is presented below.

HTI Run CMSL-8 Background

A diagram of HTI's bench unit 227 as configured for Run CMSL-8 (also known as Run 227-85) is shown in Figure 1.³ CONSOL analyzed feed samples, and samples from sample points 4 through 7, representing recycle and product streams. The operating conditions and process performance summary for the run are given in Table 1.³ Operating performance was good early in the run, but as the run continued, the catalyst age increased, and the concentration of polyethylene in the feed was increased. The resid conversion decreased as the run progressed. Several adjustments were made to process conditions after period 16 to maintain performance and operability. Notable events were: the change from coal operation in period 6 to 75% coal and 25% mixed plastics prior to period 11; the increase in second-stage reactor temperature from 830 to 850 °F, an increase in first-stage space velocity from 30 to 40 lb dry feed/hr/ft³ reactor prior to period 16; the increase in mixed plastics concentration to 33%, decrease in space velocity from 40 to 30 lb dry feed/hr/ft³ reactor, and increase in dispersed Mo catalyst concentration from 100 to 200 ppm, prior to period 20; and, prior to period 22, the switch from 33% mixed plastics to 33% HDPE. Over the duration of the run, the supported catalyst reached an age of 966 lb dry feed/lb cat. Samples received as either period 22 or period 23 samples were considered to represent material balance period 22.

Analyses Performed

A brief description of the Run CMSL-8 samples and analyses conducted as CONSOL's baseline characterization is provided in Table 2. In this paper, the samples will be referred to by the abbreviations given in Table 2, e.g., SOH for the product oil, PFL for the recycle liquid, and PFC for the bottoms stream. The baseline analytical methods can be applied to many different kinds of samples, can be performed quickly, and have proven to be suitable for liquefaction process stream characterization. In addition to the routine laboratory analyses, non-routine characterization (such as FTIR characterization of certain samples) was performed, based on the Run POC-2 sample experience. Several samples were selected for specialized analyses, such as plasma desorption mass spectrometry (PDMS) and field ionization mass spectrometry (FIMS).

SOH Product Characteristics and Effects of On-line Hydrotreating

The separator overheads (SOHs) from periods 6 and 11 through 23 were consistently low in aromatic hydrogen and high in paraffinic hydrogen content (Figure 2). There was a small increase in paraffinic hydrogen from periods 16 to 20 to 23

coincident with increases in the HDPE concentration in the feed (8.75 to 11.5 to 33 wt % dry feed in those periods). There was no change in paraffinic hydrogen content from period 6 (coal-only) to period 11 (coal/mixed plastics). However, a substantially lower paraffinic hydrogen content was observed when the on-line hydrotreater was by-passed in period 9. This indicates that, because of extensive upgrading in the hydrotreater, the paraffinic hydrogen content of the SOH may be relatively insensitive to other process changes. The product oil (SOH) sample from period 9, in which the on-line hydrotreater was by-passed, is much poorer in quality than the SOHs produced with the hydrotreater in place. Differences included: medium brown in color vs. colorless, presence of a "coal liquid" odor, more aromatic, less paraffinic, and considerably higher phenolic - OH concentration (Figure 2). The effects of hydrotreating observed in this run were greater than those observed in Run POC-2.¹ This may be because the distillate hydrotreated in Run CMSL-8 is a thermal distillate, and the distillate of Run POC-2 came from a catalytic reactor.

Gas chromatography-mass spectrometry (GC-MS) total ion chromatograms of SOH samples (Figure 3) show that replacing a portion of the coal with mixed plastics (from period 6 to period 11) and the switch from mixed plastics to HDPE (from period 11 to period 22) increased the concentrations of n-paraffins in the SOHs, and shifted the n-paraffins to higher molecular weight. Thus, HDPE appears to be an important source of the n-paraffins in the SOHs produced after period 6. Two peaks corresponding to ethylbenzene and cumene (isopropylbenzene) are marked in Figure 3. These components are polystyrene (PS) liquefaction products. Cumene was not found in the coal-only period SOH, and ethylbenzene was present at about 1% concentration in the coal-only and coal/HDPE periods 6 and 23. ¹H-NMR results indicate that PS products persisted in the SOH product from the coal/HDPE period. In the NMR spectra of the SOHs, ethylbenzene features are nonexistent in the coal period SOH, quite prominent in the coal/mixed plastics period SOHs, and observable, but small, in the coal/HDPE period SOH.

The PS products were quantified by GC-MS and ¹H-NMR (Table 3). The area of the ethylbenzene and cumene peaks, as a percentage of the total ion chromatogram was used to estimate the concentration of these components in the SOHs. The alkylbenzene concentration of the SOHs was estimated (as ethylbenzene) by integration of the ¹H-NMR peak near 7.1 ppm. Based on these estimates, ethylbenzene and cumene constitute about 8-15 wt % of the coal/mixed plastic period SOHs (with the HTU in use), less than 1 wt % of the coal/HDPE period SOH, and about 2 wt % or less of the coal period SOH. When the hydrotreater was by-passed with the coal/mixed plastics feed, the concentration increased to about 15 to 23 wt % of the SOH. Approximately 50% of the PS fed to the process can be accounted for as these alkylbenzene products (with the hydrotreater operating).

HDPE in Recycle and Resid Samples

The PFLs from the coal/plastics periods 11, 16, 20, and 22 contained 15 to 30 wt % THF insolubles. These insolubles were tan with white specks early in the run and dark brown later in the run. The presence of THF insolubles in the PFL is a unique feature of coal/plastics processing. PFLs from coal-only operations (including period 6 of this run) typically contain little or no THF-insoluble material. The FTIR spectra of insolubles from coal/plastics periods 11 and 22 were similar and indicated that they are polyethylene-like material (Figure 4). PFL 850 °F distillation bottoms from two of three coal/mixed-plastics periods separated into two solid phases upon cooling; none of the other PFL resids behaved in this way. The two phases differed in physical characteristics and

color. Diffuse reflectance FTIR (Figure 4) was used to examine both phases of one of the resids. The upper phase appeared to be predominantly plastic derived (much of it PE), and the lower phase is predominantly coal derived. The spectrum of the upper brown phase indicated primarily aliphatic hydrocarbons with PE-like features. Aromatic hydrocarbon peaks also were significant, but no features indicated the presence of heteroatomic functional groups. The spectrum of the lower black phase showed more intense aromatic hydrocarbon peaks than did the upper phase, and a significant amount of aliphatic hydrocarbon in the lower phase, but no distinctive PE-like features. The spectrum of the lower phase also contains prominent peaks from heteroatomic functionality, perhaps N-H and O-H.

Samples of both PFL resid phases, along with other samples from Run CMSL-8, also were characterized by field-ionization mass spectrometry (FIMS) at SRI International.⁴⁻⁶ The pyrolysis profiles are shown in Figures 5a-b and the FIMS spectra in Figures 5c-h. Volatilization of each sample was nearly complete. The pyrolysis profiles show that HDPE pyrolyses to low molecular weight components at about 430 °C (Figure 5a), and that the THF-insoluble sample from the period 22 PFL is nearly all HDPE (Figure 5b). In the mass spectra, the HDPE pyrolysis products are lower in molecular weight and generally distinct from the coal-derived resid components (Figure 5c-h). These spectra also confirm the identification of the period 22 PFL THF insolubles as nearly pure HDPE (Figure 5c-d), and show that HDPE is present to varying degrees in the other samples from coal/plastic operating periods (Figure 5c-h). The plastic layer (Figure 5g) contains more HDPE than the corresponding coal layer (Figure 5h). Furthermore, the odd/even mass ratio is higher for the coal layer, suggesting that it contains more heteroatomic species. This is consistent with the FTIR results. A simple quantitation method was tried with the FIMS data (Table 4), and it appears to work fairly well (to the extent determinable at this stage). This method is compared with another method below.

In Table 5, the results of two methods for estimating the concentration of HDPE in liquefaction process streams are compared. In the first method, the THF-insoluble content of a PFL sample was measured and assumed to be unconverted HDPE. In the second method, a linear relationship between the HDPE concentration and the number average molecular weight (M_n) determined by FIMS was assumed. The methods for this limited sample set agree quite well. The FIMS approach offers the potential to quantify the amount of unconverted HDPE present in the bottoms (PFC) stream. This would allow a more accurate determination of HDPE conversion than is presently available.

Conversion of HDPE During Run CMSL-8

CONSOL and others have found indications that high-density polyethylene (HDPE) is less reactive than coal and other plastics feedstocks toward liquefaction at conventional liquefaction conditions. Since adequate conversion of HDPE is an important factor in the development of coal/plastics coprocessing, it is important to know the conversion of the HDPE during Run CMSL-8 and other coal/plastics coprocessing runs. Upper limits for both single-pass and overall conversions of HDPE during Run CMSL-8 were estimated (Table 6). It was assumed that: 1) the HTI unit was operating at steady-state, 2) that the PFL THF-insolubles are HDPE, and 3) that there was no unconverted HDPE in the PFC. During Run CMSL-8, PFL was both the recycle liquid (Figure 1) and a liquid product. Overall conversion is a measure of fresh HDPE which is not present as unconverted HDPE in the net products; in overall HDPE conversion, recycled HDPE is considered an internal stream and does not need to be explicitly accounted

for. The single-pass conversion of HDPE is a measure of the disappearance of both the recycled and fresh HDPE fed (recycled HDPE is explicitly accounted for).

The conversion calculations require material balance data for the HTI run periods,³ and an estimate of the amount of HDPE in the pressure-filter liquid (PFL). Details of the method used are provided elsewhere.⁷ These results (Table 6) represent an upper limit for conversion, because the HDPE concentration in the pressure-filter cake (PFC) product could not be determined. The overall conversion of HDPE ranged from 40-80% during the run (Table 6), lower than the 90-95% coal conversion and 80-85% resid conversion typically observed for coal liquefaction. The single-pass HDPE conversions averaged around 25%. Both overall and single-pass conversions were lowest during period 16, after an increase in second-stage reactor temperature and space velocity. Measures taken by HTI to improve performance after period 16, such as reducing the space velocity and doubling the dispersed Mo catalyst concentration, restored the conversions observed in period 11. The single-pass HDPE conversion in period 22 was much higher at about 50%. Measures that HTI took to maintain operability in that period of the run when HDPE and coal were fed seemed to provide the high single-pass conversion, and high overall conversion of HDPE.

Conclusions

The major conclusions from characterization of Run CMSL-8 samples are listed below.

- PS products are identifiable and quantifiable in the SOH distillate product from coal/mixed plastics co-liquefaction.
- HDPE appears to be an important source of n-paraffins in the SOHs from coal/plastics co-liquefaction.
- The SOH sample from period 9 in which the on-line hydrotreater was bypassed was much poorer in quality than the SOHs produced with the hydrotreater in operation.
- Identification of some PS and polyethylene terephthalate (PET) products in the SOHs may be masked by highly effective on-line hydrotreating. Addition of a hydrotreater feed sample point, or of more off-line hydrotreater reference periods may help in identification of plastics liquefaction components in the SOHs.
- Incompletely converted HDPE constituted 15 to 30 wt % of the PFL recycle streams, and was found as THF insolubles; virtually no THF insolubles were present in the coal-only period PFL.
- Phase separation in some PFL distillation resids indicates that HDPE products have complex phase behavior.
- HDPE conversions were estimated to be ca. 80 % overall, and ca. 25 % single-pass, and the conversions were responsive to changes in process conditions.
- THF insolubility is currently the best way to separate HDPE in liquid samples which contain no other solids.
- FTIR is useful for the identification of HDPE products.
- FIMS allows distinction of coal-derived material and HDPE-derived material in process stream samples. Quantification of HDPE seems possible using the FIMS technique, but additional development is needed.

PLANS:**CONSOL Support to DOE Coal/Plastics Co-Liquefaction Development**

We will do similar sample collection, distribution, and characterization work for future runs. Specialized analyses will supplement baseline characterization techniques. Additional analytical work, such as method development and evaluation, will be performed, as needed, to address key issues in coal/waste coprocessing. This will include evaluation of methods for characterization of plastic liquefaction products. Additional work could include development of alternative liquefaction work-up schemes to accommodate plastic components which are not amenable to conventional coal liquefaction work-up schemes. It is anticipated that at some future point, a distillate product oil from coal/waste co-liquefaction will be selected by DOE for a full set of product inspection tests. CONSOL will assist DOE in conducting these tests.

ACKNOWLEDGEMENTS:

The assistance of several individuals is greatly appreciated. These include Lorna Schlutz, Sophia Heunisch, and Dave Olson at CONSOL R&D, Vivek Pradhan at HTI, Udaya Rao and Kurt Rothenberger at DOE/PETC, John Larsen at Lehigh University, and Ripu Malhotra at SRI.

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**TABLE 1. RUN CONDITIONS AND PROCESS PERFORMANCE SUMMARY
FOR HTI RUN CMSL-8 (227-85)**

Condition	1	2	3	4	5
Period No.	6	11(b)	16	20	22
Hours of Run (End of Period)	144	264	384	480	528
wt % Plastics in Feed (a)	0	25	25	33	33
Stage 1 Cat. Age, lb Feed/lb Cat	252	457	711	884	966
Stage 1 Feed Space Velocity lb Feed/hr/ft ³ Reactor Vol.	32.2	29.6	39	30.1(c)	29.6
Oils/Solids Ratio	1.5	1.6	1.8	2.1	1.9
<u>Temperature, °F</u>					
Stage 1	810	810	810	810	810
Stage 2	830	830	850	850	850
HTU	715	715	715	715	715
Dispersed Mo Concentration, ppm of					
Dry Feed	100	100	100	200(c)	200
Total Material Recovery, % (Gross)	102.2	98.4	96.7	101.2	99.6
<u>Estimated Normalized Yields, wt % MAF Feed</u>					
C ₁ -C ₃ in Gases	11.35	9.14	9.02	7.41	5.17
C ₄ -C ₇ in Gases	4.81	3.27	3.41	3.17	3.27
IBP-350 °F	15.86	20.48	19.00	17.63	8.80
350-500 °F	17.99	12.57	8.59	11.16	7.60
500-650 °F	21.14	19.85	12.27	16.88	10.72
650-850 °F	10.18	11.84	15.18	11.54	14.24
850-975 °F	2.29	2.94	5.60	4.22	6.43
975 °F	4.74	10.53	17.15	19.67	33.83
Unconverted Feed	3.90	4.07	4.50	4.40	4.22
Water	9.04	7.34	6.90	5.92	4.85
COx	0.67	0.80	0.86	0.57	0.16
NH ₃	1.50	1.08	1.04	0.82	0.27
H ₂ S	3.98	2.98	2.84	2.52	2.24
Hydrogen Consumption	7.46	6.91	6.35	5.71	1.80
<u>Process Performance</u>					
Feed Conversion, wt % MAF Feed	96.10	95.90	95.50	95.60	95.80
975 °F ⁺ Conversion, wt % MAF Feed	91.40	85.40	78.40	75.90	62.00
C ₄ -975 °F Distillates, wt % MAF Feed	72.30	71.00	64.00	64.40	51.00
Hydrogen Efficiency, lb Dist/lb H ₂	9.69	10.27	10.08	11.28	28.33

Feeds:

Illinois No. 6 Crown II Mine coal, HDPE, Polystyrene, and PET

Back Pressure: 2500 psig

Catalysts:

K-1: Shell 317 Supported + Dispersed Sulfated Fe/Mo Oxide (100 ppm Mo)

K-2: Only Dispersed Sulfated Fe/Mo Oxide Introduced in Feed to K-1

Hydrotreater: HRI-6135 (Criterion C-411 Trilobe)

- (a) Conditions 2-4 used a 50/35/15 w/wt % ratio of HDPE/PS/PET; Condition 5 used HDPE alone w/coal.
- (b) Although not specifically listed here, in period 9 the on-line hydrotreater (HTU) was by-passed; otherwise conditions were the same as in period 11.
- (c) The total space velocity was reduced from 40 to 30 beginning in Period 18 as a result of operating difficulties at higher space velocities; the dispersed catalyst addition rate also was increased from 100 ppm Mo to 200 ppm Mo beginning in Period 19 to improve process performance.

**TABLE 2. CONSOL ANALYSES OF SAMPLES
FROM HTI COAL/PLASTICS CO-LIQUEFACTION RUN CMSL-8**

Sample Description; Name (Abbrev.); Sample Point	Periods	Technique & Information Sought (Refer to Key)
Product Distillate; Separator Overheads (SOH); SP-4	6,9,11,16,20,23	A,B,C
Recycle Oil; Pressure Filter Liquid (PFL); SP-6	6,11,16,20,22	A,E,F,G; THF Extract - B; THF Insol - D; Dist. - A,B,E; Resid - G; Resid THF Extract - A,B,H
Solid Residue; Pressure Filter Cake (PFC); SP-7	6,11,16,20,22	G; THF Extract -A,B,H

KEY TO TECHNIQUES AND INFORMATION SOUGHT:

- A** = ¹H-NMR for hydrogen distribution (7 classes), aromaticity (degree of hydrogenation), paraffinicity, hydrogen donors
- B** = FTIR in THF solution for phenolic -OH content
- C** = GC-MS for composition, carbon numbers of paraffins
- D** = special analyses
- E** = microautoclave test with standard coal for donor solvent quality
- F** = 850°F distillation for distillate content
- G** = THF extraction and ash for resid, ash and IOM content, for coal and resid conversion
- H** = solvent fractionation (oils, asphaltenes, preasphaltenes) for resid composition.

TABLE 3. QUANTITATION OF POLYSTYRENE LIQUEFACTION PRODUCTS IN SOH PRODUCT OILS FROM HTI RUN CMSL-8

Period	Analysis by GC-MS, Area % of SOH Total Ion Chromatogram			Analysis by ¹ H-NMR		SOH Yield, wt % of Dry Feed	EB+IPB by GC-MS, as wt % of PS Fed	EB by ¹ H-NMR, as wt % of PS Fed
	Ethylbenzene, Ref. Time ca. 16.7 min.	Cumene (Isopropylbenzene), Ref. Time ca. 21.8 min.	Total, Area % (assumed to equal wt % of SOH)	As Ethylbenzene, wt % from Integration of Peak at 7.1 ppm	wt % PS in Dry Feed			
6 (Coal)	0.55	-	0.55	-	0	50.06	- (b)	-
11 (Coal/Mixed Plastics)	6.53	1.91	8.4	8.8	8.75	47.65	45.7	47.9
16 (Coal/Mixed Plastics)	8.32	3.38	11.7	15.1	8.75	33.52	44.8	57.8
20 (Coal/Mixed Plastics)	6.94	2.01	9.0	12.1	11.55	43.28	33.7	45.3
23 (Coal/HDPE)	1.38	0.29	1.7	3.4	0	25.29	(c)	(d)
9 (Coal/Mixed Plastics - HTU Off-line)	13.52	4.03	17.6	15.4 (a)	8.75	35.02	70.4	61.6

- (a) Assumed 11 wt % H in SOH for NMR estimate, other periods used wt % H reported by HTI.³
 (b) Represents 0.3 wt % of dry coal fed; equivalent to 3.1 wt % of PS fed in period 11.
 (c) Represents 0.6 wt % of dry coal fed; equivalent to 3.7 wt % of PS fed in period 20.
 (d) Represents 1.2 wt % of dry coal fed; equivalent to 7.4 wt % of PS fed in period 20.

TABLE 4. ESTIMATION OF HDPE CONCENTRATION WITH FIMS DATA

Sample	FIMS M_n , Da	FIMS M_w , Da	Estimate of wt % HDPE ^(a)	M_w/M_n
HDPE	154	558	100	3.6
PFL 22 THFI ^(b)	184	662	93	3.6
PFC 22	304	591	66	1.9
PFL 22	329	493	14 ^(c) (61 ^(d))	1.5
PFL 11 Resid Top Layer	404	627	44	1.6
PFL 11 Resid Bottom Layer	466	580	30	1.2
THF-Soluble Coal Resids ^{4,5}	600	710	-	1.2

Note: FIMS analyses were performed by R. Malhotra, at SRI International.

- (a) It was assumed that wt % HDPE is linearly related to M_n , and that $M_n = 154$ Da for 100% HDPE, and $M_n = 600$ Da for 100% coal resid.^{4,5}
- (b) THFI = THF insolubles.
- (c) It was assumed that $M_n = 515$ Da for the non-HDPE portion of the sample, rather than 600 Da, as in the other samples. This value was calculated from 21.1 wt % of the THF-soluble PFL as 850 °F distillate with an assumed $M_n = 200$ Da, and 78.9 wt % of the THF-soluble PFL as 850 °F resid with an assumed $M_n = 600$ Da.
- (d) Value if uncorrected for 850 °F distillate.

TABLE 5. COMPARISON OF METHODS TO ESTIMATE HDPE CONCENTRATION

Sample	Estimate of HDPE as THF Insolubles, wt % of Sample		Estimate of wt % HDPE, Based on M_n
	From Whole Sample	From Resid	
PFL 22 THFI	100	-	93
PFL 22	18.6	15.8	14
PFL 11 Resid Top Layer	-	-	44
PFL 11 Resid Bottom Layer	-	-	30
PFL 11	20.0	20.3	23 ^(a)

- (a) Calculated from wt % HDPE in each resid layer, the wt % of each layer in the resid (66.7 wt % top layer, 33.3 wt % bottom layer), and 59.3 wt % resid in the PFL.

TABLE 6. OVERALL AND SINGLE-PASS CONVERSIONS OF HDPE DURING HTI RUN CMSL-8

Period	wt % HDPE in PFL ^(a)	Overall Conversion, % ^(b)	Single-Pass Conversion, % ^(b)
Using THF insolubles in whole PFL as estimate for HDPE in PFL:			
11	20.0	80.7	23.2
16	30.4	44.6	9.1
20	14.5	71.6	26.2
22	18.6	73.9	49.5
Using THF insolubles in PFL resid as estimate for HDPE in PFL:			
11	20.3	80.5	22.9
16	37.4	32.0	5.9
20	16.5	67.7	22.9
22	15.8	77.8	53.3

(a) Assuming that THF insolubles in PFL are unconverted HDPE.

(b) Calculations are described in Reference 7.

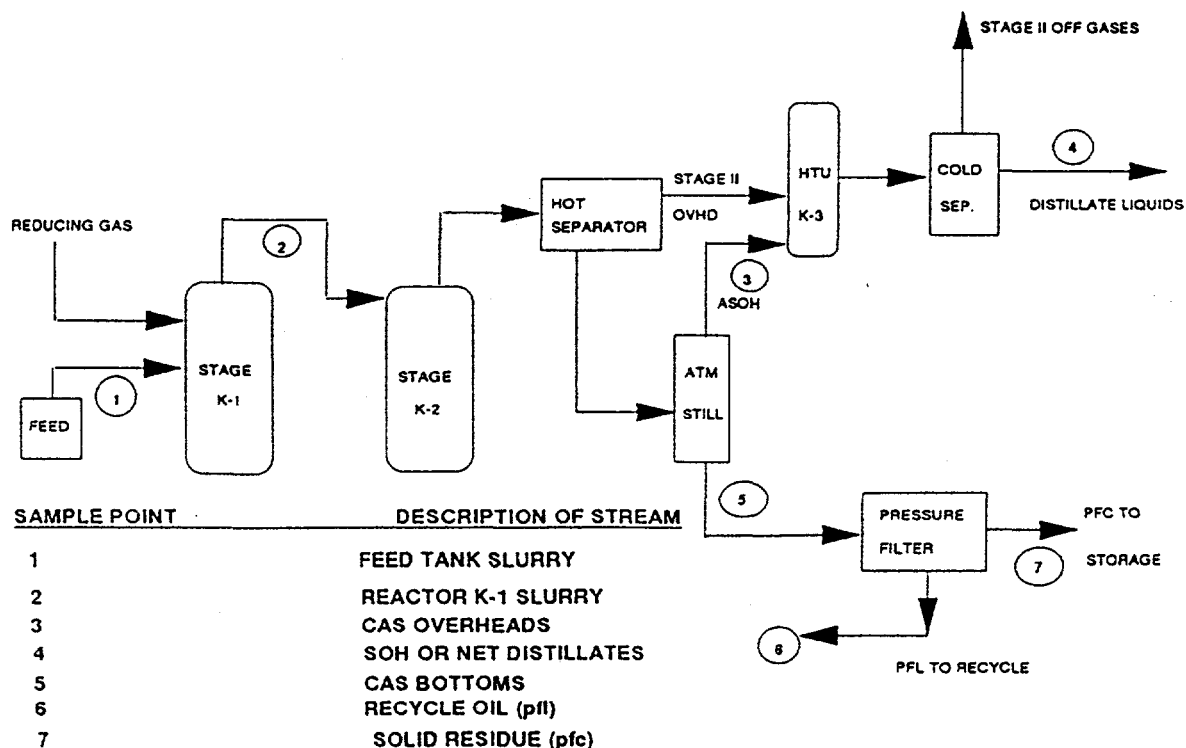


Figure 1. Simplified Plant Diagram for HTI Run CMSL-8.
(Source: Reference 3)

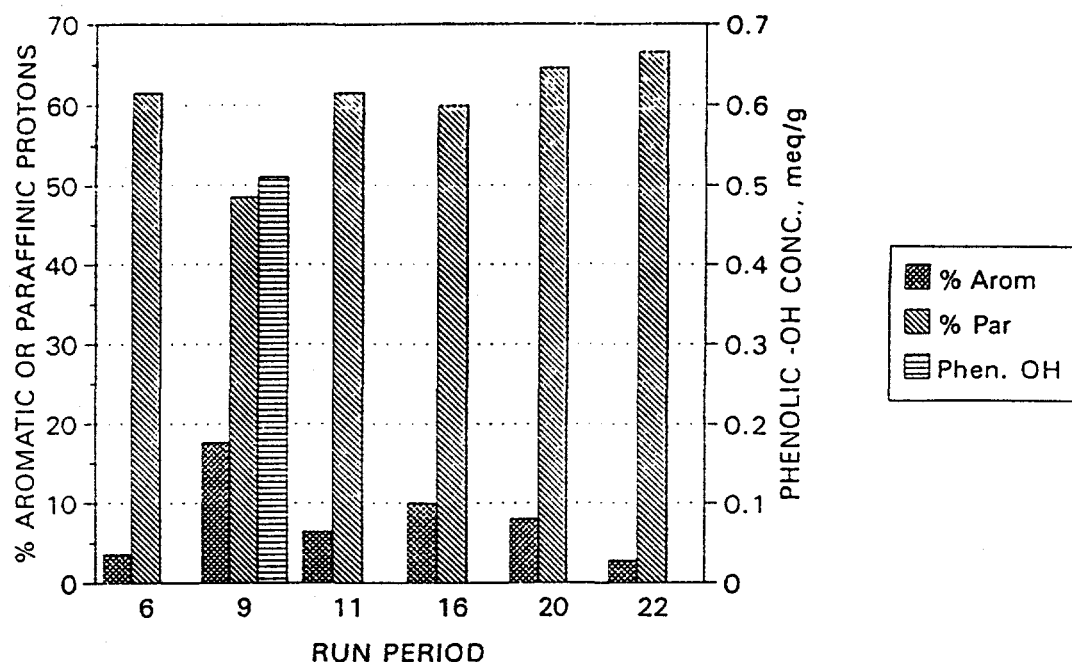


Figure 2. Characteristics of SOH Samples from Run CMSL-8.

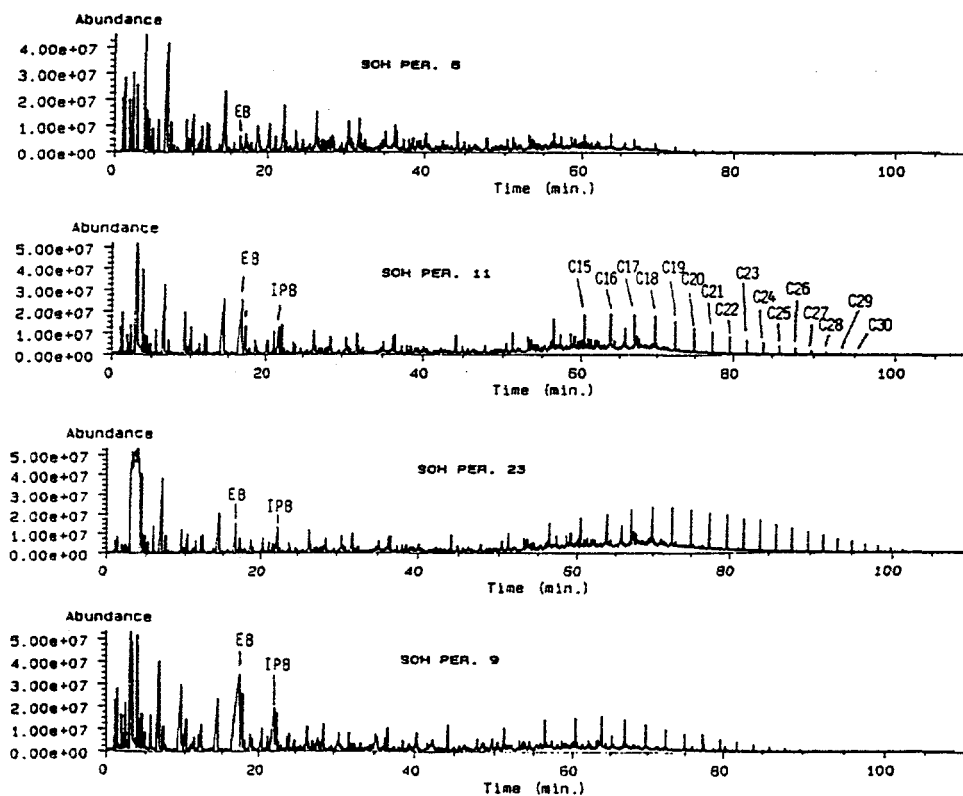


Figure 3. Gas Chromatography-Mass Spectrometry (GC-MS) Total Ion Chromatograms of Selected SOH Samples from Run CMSL-8.

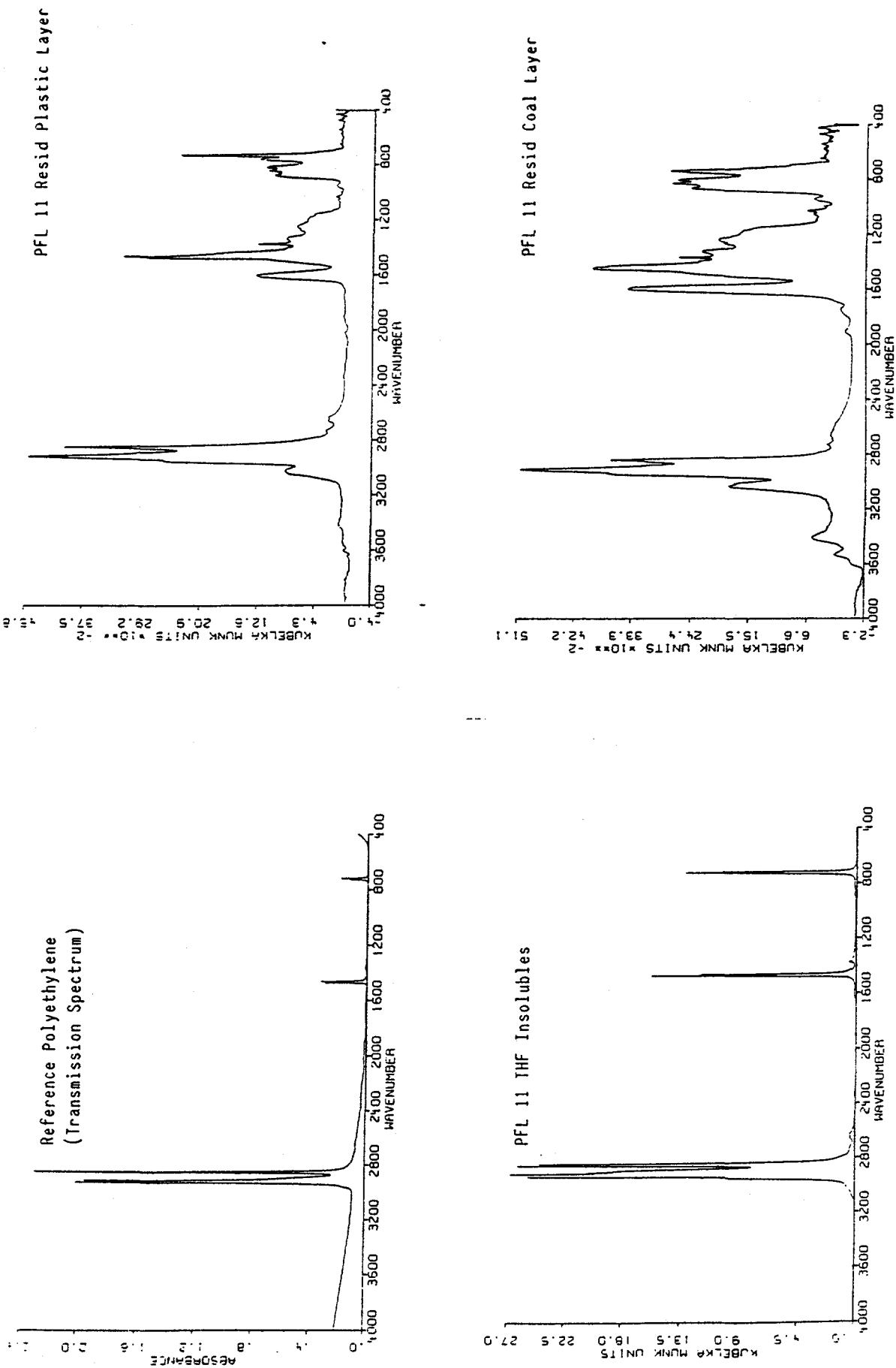
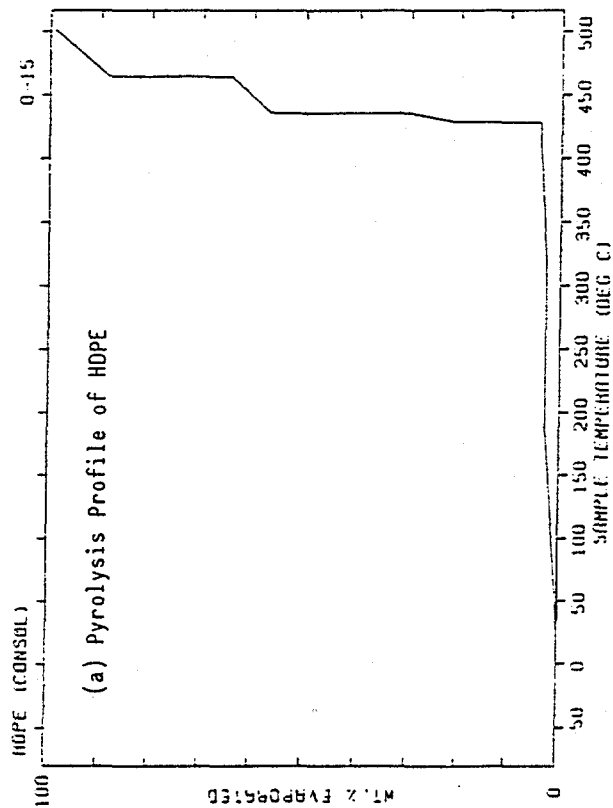
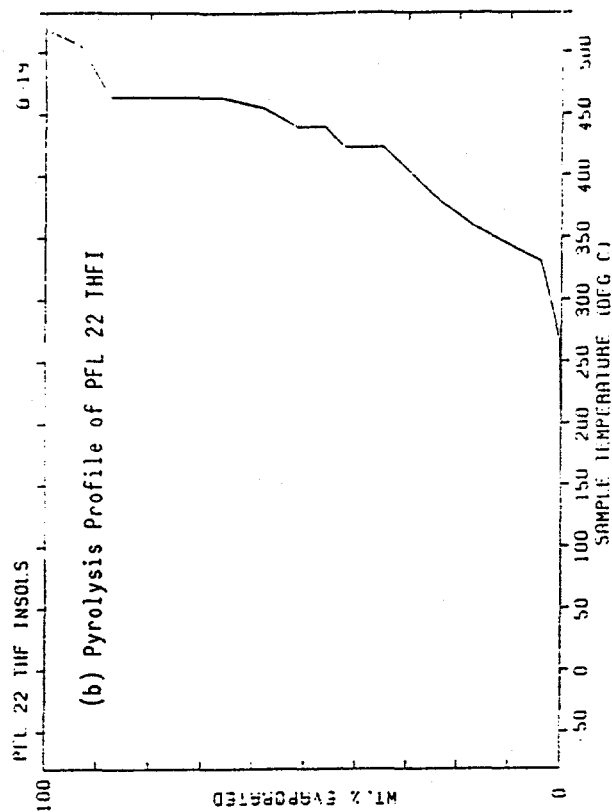


Figure 4. Fourier-Transform Infrared (FTIR) Spectra of Reference Polyethylene and Selected Run CMSL-8 Samples.

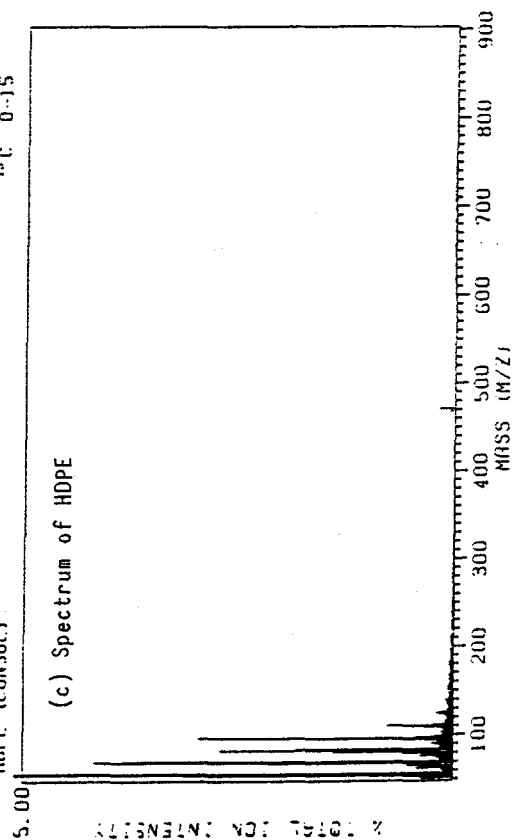
HDPE (CONSOL) FIMS VACUUM EVAPORATION CURVE



PTL 22 THF INSOL'S FIMS VACUUM EVAPORATION CURVE



HDPE (CONSOL) R10906.SUM 1 = 28 10 501 DEG C N OV MW=154 WT OV MW=558 13C 0-15



PTL 22 THF INSOL'S R10903.SUM 1 = 28 10 517 DEG C N OV MW=184 WT OV MW=662 13C 0-19

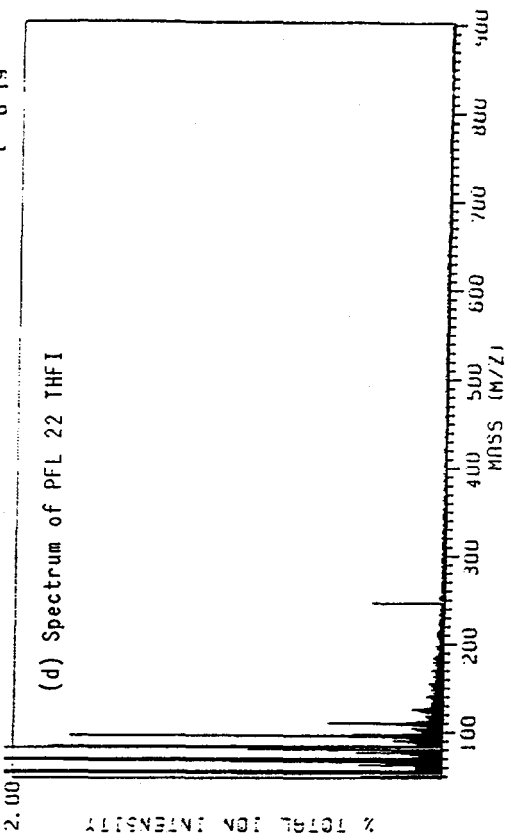


Figure 5. Pyrolysis Profiles and Field-Ionization Mass Spectrometry (FIMS) Spectra of Selected Run CMSL-8 Samples.

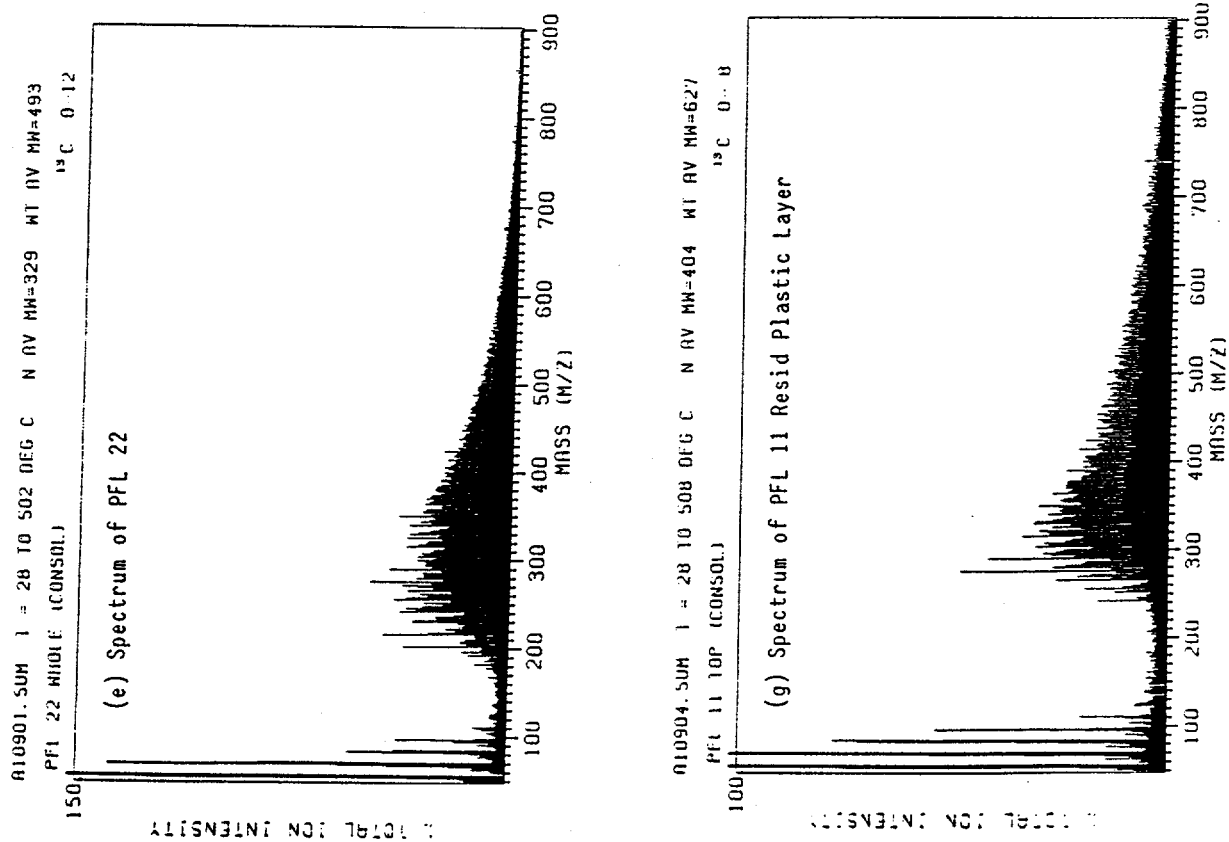
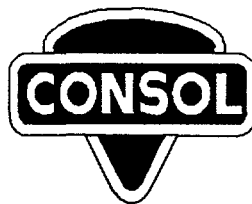


Figure 5 (Continued). Pyrolysis Profiles and Field-Ionization Mass Spectrometry (FIMS) Spectra of Selected Run CMSL-8 Samples.

Appendix 6

DOE REFINING AND END-USE PROJECT PRESENTATION

INSPECTION OF NET PRODUCTS OF HTI RUNS POC-1 AND POC-2



R. A. Winschel

Presented at Refining and End Use Review Meeting
San Antonio, TX
November 14, 1995
DOE Contract DE-AC22-94PC93054

PURPOSE OF WORK

- Inspection of liquefaction products of DOE-supported operations
- In conjunction with Burns and Roe Services Corp.
- Better define value and refining requirements of coal liquids

CONSOL'S PAST INSPECTIONS

- Samples inspected earlier
 - Wilsonville Run 259G net product
Pittsburgh Seam, C/C
 - Wilsonville Run 260D net product
Black Thunder Mine, C/T
 - HTI Run CC-15 net product
Black Thunder Mine, T/C
 - HTI Run CMSL-2 net product
Illinois 6 Seam, C/C
- Inspection of crude and fractions
- Caustic wash, re-inspection, analysis of phenols

CONSOL'S RECENT INSPECTIONS

- HTI RUN POC-1
Illinois 6 Seam, C/C/(HTR)
- HTI Run POC-2
Black Thunder Mine, C/C/HTR
- 6 gal each supplied by Southwest Res. Inst.
- Testing at Conoco Inc.
and Phillips Petroleum Co.
- Inspected crude and fractions
- Identical testing protocol for both samples

CRUDE OIL CHARACTERISTICS

Property	POC-1	POC-2
GRAVITY, °API	32.2	33.7
90% off @, °F (°C)	582 (306)	592 (311)
C, wt%	86.9	86.8
H, wt%	12.6	13.1
N, wt%	0.058	0.006
O, wt%	0.2	<0.1
S, wt%	0.049	0.008
ash, wt%	0.00	0.00
V, ppm	<1	<1
Ni, ppm	<0.5	<0.5
Fe, ppm	3.7	<0.5
Cu, ppm	<0.5	<0.5
Zn, ppm	<1	<1

FRACTIONATION OF CRUDES

Yields in wt%

Cut point, °F	POC-1	POC-2
IBP - 180, naphtha	4.5	4.5
180 - 350, naphtha	22.8	24.8
350 - 400, swing cut	8.2	9.0
400 - 500, diesel fuel	21.9	22.0
500 - 550, diesel fuel	15.5	14.3
550 - 650, fuel oil	20.8	20.8
650+, atm. resid	5.6	3.9

NAPHTHA CHARACTERISTICS

IBP - 180°F plus 180 - 350°F Fractions

Property	POC-1	POC-2	Gasoline A Specs ASTM D439-88
°API	50.0	51.3	
N, wt%	0.020	<0.001	
S, wt%	0.043	0.001	0.10 max
90% off @, °F	ca. 315	ca. 315	374 max
RVP, psi	2.1	1.8	9 max
Cu Corrosion	1A	1A	1 max
Existent Gum, mg/100 mL	14.8	3.6	5 max
Ox. Stability, h	16	16	4 min
Paraffins, vol%	19.6	20.4	
Naphthenes, vol%	65.3	67.2	
Aromatics, vol%	10.1	7.1	
Benzene, vol%	0.46	0.28	
RON	65.1	59.5	
MON	62.5	59.0	

Some properties calculated as weight/volumetric avg. of fractions

SWING CUT CHARACTERISTICS

350 - 400°F Fraction

Property	POC-1	POC-2	Jet A-1 Specs ASTM D1655-88
°API	34.2	36.3	37 - 51
Kin. Visc. @ -4°F	4.35	4.12	8 max
Freezing Pt., °F	<-60	<-60	-53 max
10% off @, °F	369	361	400 max
FBP, °F	386	394	572 max
H, wt%	12.6	13.2	
N, wt%	0.059	0.002	
S, wt%	0.036	0.003	0.3 max
Mercaptan S, wt%	0.007	<0.001	0.003 max
Smoke Pt., mm	13.7	17.7	25 (20) min
Naphthalenes, vol%	1 wt%	0.11 wt%	3 max
Luminometer No.	27.2	38.0	45 min
Olefins, vol%	3.8	1	5 max (Jet B)
JFTOT	Fail/4	Fail/4	25/3 min
Cu Corrosion	1A	1A	1 max
Existent Gum, mg/100 mL	16.8	1.2	7 max
Acidity, mg KOH/g	0.01	0.01	0.1 max
Net Heat Val., Btu/lb	18120	18350	18400 min
Cetane Index	20.6	21.8	

DIESEL FUEL CHARACTERISTICS

400 - 500°F Plus 500 - 550°F Fractions

Property	POC-1	POC-2	Diesel No. 1 Specs ASTM D975-81	Diesel No. 2 Specs ASTM D975-81
°API	26.4	28.0		
H, wt%	12.0	12.6		
N, wt%	0.061	0.009		
S, wt%	0.027	0.002	0.50 max	0.50 max
90% off @, °F	ca. 527	ca. 515	550 max	540 - 640
Flash Pt., °F	209	203	100 min	125 min
Kin. Visc. @ 104°F	2.7	2.7	1.3 - 2.4	1.9 - 4.1
Cu Corrosion	1A	1A	3 max	3 max
Cetane Index	29.0	30.5	40 min	40 min

Properties calculated as weight avg. of fractions

FUEL OIL CHARACTERISTICS

550 - 650°F Fraction

Property	POC-1	POC-2	No. 2 Fuel Oil Specs ASTM D396-80	No. 4 Fuel Oil Specs ASTM D396-80
°API	21.8	22.1	30 min	
H, wt%	11.9	12.3		
N, wt%	0.053	0.006		
S, wt%	0.018	0.001	0.5	
Flash Pt., °F	>250	>240	100 min	130 min
Pour Pt., °F	-5	-5	-6 max	20 max
90% off @, °F	604	610	540 - 640	
Kin. Visc. @ 104°F	7.2	7.8	1.9 - 3.4	5.5 - 24.0

CHARACTERISTICS OF ATMOSPHERIC RESID

650°F+ Fraction

Property	POC-1	POC-2
°API	18.7	20.4
H, wt%	11.6	12.2
N, wt%	0.13	0.013
S, wt%	0.061	0.009
Concarb, wt%	0.4	0.04
Kin. Visc. @ 210°F	3.7	3.5

SUMMARY OF INSPECTIONS

HTI RUNS POC-1 AND POC-2

- Both crudes
 - very low S, N
 - <6% atmospheric resid
 - nearly devoid of metals
 - approximate yields:
 - 30% IBP - 350°F
 - 10% 350 - 400°F
 - 35% 400 - 550°F
 - 25% 550°F+
- Fractions of both crudes have excellent
 - oxidation stability
 - Cu corrosion
 - acidity
- Fractions of both crudes have low API gravity relative to b.pt.; high concentration of cyclic compounds
- POC-2 fractions, relative to POC-1 fractions
 - higher H, API gravity, smoke pt., luminometer no.
 - lower heteroatoms, aromatics, olefins, gum, octane
- Both crudes make excellent refinery feedstocks/blendstocks